



Catalytic oxidation of gaseous reduced sulfur compounds using coal fly ash

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Abstract

Activated carbon has been shown to oxidize reduced sulfur compounds, but in many cases it is too costly for large-scale environmental remediation applications. Alternatively, we theorized that coal fly ash, given its high metal content and the presence of carbon could act as an inexpensive catalytic oxidizer of reduced sulfur compounds for “odor” removal. Initial results indicate that coal fly ash can catalyze the oxidization of H₂S and ethanethiol, but not dimethyl sulfide (DMS) and dimethyl disulfide (DMDS) at room temperature. In batch reactor systems, initial concentrations of 100–500 ppmv H₂S or ethanethiol were reduced to 0–2 ppmv within 1–2 and 6–8 min, respectively. This was contrary to control systems without ash in which concentrations remained constant. Diethyl disulfide was formed from ethanethiol substantiating the claim that catalytic oxidation occurred. The presence of water increased the rate of adsorption/reaction of both H₂S and ethanethiol for the room temperature reactions (23–25 °C). Additionally, in a continuous flow packed bed reactor, a gaseous stream containing an inlet H₂S concentration of 400–500 ppmv was reduced to 200 ppmv at a 4.6 s residence time. The removal efficiency remained at 50% for approximately 4.6 h or 3500 reactor volumes. These results demonstrate the potential of using coal fly ash in reactors for removal of H₂S and other reduced sulfur compounds.

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1. Introduction

Low concentration volatile compound emissions are a major source of air pollution within many industries. High volume low concentration emissions (HVLC) from the pulp and paper industry, rendering industry, composting operations, and waste-water treatment facilities, e.g. contain a range of reduced sulfur compounds (e.g. H₂S and dimethyl sulfide (DMS))

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that are odorous, toxic at high concentrations, and can contribute to smog formation [1]. Incineration, regenerative thermal oxidation (RTO), and wet scrubbers are the current air pollution control technologies used to treat the reduced sulfur fraction in many emissions [2,3]. RTOs have high operating costs, produce a greenhouse gas (CO_2), and require SO_2 scrubbing (if sulfur is present). Wet scrubbers require costly oxidizing chemicals (e.g. ClO_2) and can produce chlorinated hydrocarbons if not properly controlled. Environmentally benign and cost effective air pollution control technology of reduced sulfur compounds is required for many agricultural and wood industries.

Adsorption processes using activated carbon are used in many cases to remove a wide range of volatile organic and inorganic compounds from gaseous emissions and has been used to buffer biofilters from VOC perturbations [4]. Moreover, activated carbon is reported to oxidize H_2S over a temperature range from ambient to 250°C [5,6]. Surface oxides have been suggested to be the active centers where oxidation takes place [7]. It has been theorized that in a heterogeneous environment, sorption of oxygen and H_2S is required and that elemental sulfur is produced unless water is available for SO_2 reduction. The mechanism appears to be a function of temperature and moisture levels. At temperatures below 50°C , water was required for complete H_2S oxidation [7,8]. At temperatures below 100°C , water is reported to enhance H_2S oxidation, but the presence of water reduces H_2S conversion at temperatures above 125°C [6].

In other studies, reactors packed with activated carbon fiber (ACF) reduced inlet H_2S concentrations from 200 to 0–2 ppmv (close to 100% conversion at a residence time of 0.6 min and 90% relative humidity), at 20°C and a moisture content of 80% for 45 days [8]. Catalytic activity was maintained by periodic washing. Dry ACF resulted in only a 12.5% conversion over the same period. Similar results were found for methanethiol (MT), if H_2S was present [9], i.e. MT was not oxidized unless H_2S was present. Similar results were reported for mixtures of H_2S , MT, and DMS [10]. When catalytic oxidation using activated carbon was coupled to a biofilter, the two-stage process was capable of removing a mixture of MT, DMS, DMDS, and H_2S for a 2.5-month period [11].

Activated carbon has also been shown to oxidize H_2S in waste-water at temperatures ranging from 8 to 24°C (conversions ranging from 60 to 100% for residence times ranging from 8 to 11 min [12]). Recently, coal fly ash was shown to oxidize sodium sulfide (Na_2S) due to the presence of non-metallic and metallic oxides [13]. The presence of metal ions in pulp mill waste-water significantly enhanced hydrogen sulfide oxidation upon aeration [14]. Although, activated carbon has both, a high adsorption capacity and potential catalytic activity towards reduced sulfur compounds, use of activated carbon in many cases is limited due to its high cost.

Given these data, it was theorized that coal fly ash could act as a low temperature adsorbent/catalytic oxidizer of reduced sulfur compounds, given the potential presence of activated carbon and metal oxides in its matrix. If feasible, we envision that the ash could be incorporated in or on an inert matrix and used in different reactor designs for reduced sulfur compound removal in the rendering industry or pulp and paper industry. The adsorbent/catalyst could be periodically regenerated via heat or washing and the process could be coupled with other physical or biological processes for complete VOC removal in an economical and energy efficient manner. The objectives of this research were to determine the feasibility of using coal fly ash to catalyze the oxidation of reduced sulfur compounds.

2. Materials and methods

2.1. Coal fly ash characterization

Ash from a process utilizing selective catalytic reduction (SCR) via NH_3 injection for NO_x removal was used in this study. The physical and chemical characteristics of the fly ash were determined and included pH [15], surface area (BET using N_2 : Nova 3000 Quantachrome, Boynton Beach, FL), bulk density, and the elemental composition. The surface area, bulk density, and pH of the ash were $7.68 \pm 0.92 \text{ m}^2/\text{g}$, $0.72 \text{ g}/\text{cm}^3$, and 11.9 ± 0.01 , respectively.

2.2. Batch reactor adsorption/oxidation

Adsorption/oxidation studies were performed in batch reactor systems consisting of 120 ml amber, serum bottles (Fischer Scientific) capped with Mininert[®] valves (Valco Instruments Co. Inc., Houston, TX). Batch reactors received a defined mass of ash (0.1, 1, or 10 g) based on bulk density measurements and the ash contacted with a known initial amount of air pollutant (5–500 ppmv and a defined injection volume) at time zero. Time zero and multiple samples thereafter, were taken via gas-tight syringes (100 μl , VICI precision sampling Inc., Baton Rouge, LA) and quantified using gas chromatography to define the rate of compound loss from the headspace and equilibrium concentration. Batch reactions were performed in triplicate.

2.3. Analytical methods

The gas phase concentration of the batch reactor headspace was analyzed using a Hewlett-Packard 5890 gas chromatograph, equipped with a 0.2 mm diameter (1.2 mm film thickness) SBP-1 sulfur column (30 m), operated with splitless injection and a sulfur chemiluminescence detector or SCD (Sievers 355, Boulder, CO). Separations were performed under isothermal conditions at 80°C , using the SBP-1 sulfur column (30 m \times 0.32 μm , Supelco, Bellefonte, PA). Standard curves were prepared from gas and liquid standards in the range of 0–500 ppmv (Scott Speciality Gases, PA). The response of the SCD was found to be linear over this range of concentrations for all sulfur compounds tested with an R^2 value of 0.98–0.99. Standards were periodically analyzed to confirm the slope of the standard curve and the detector response. Standard curves and reactor analysis were performed under identical conditions (e.g. identical injection volume of 100 μl , column, temperature).

2.4. Experimental procedure—batch reactors

A total of 14 batch reactors were randomly chosen for total volume determination. The total volume was determined by filling the reactors with water to the point of the Mininert valve and weighed, the total reactor volume was determined to be $120.92 \pm 0.52 \text{ ml}$ and this value was used in all calculations. Headspace volumes and initial gas phase concentration were calculated based on the bulk density of the ash or the volume of water added to the

reactors. A defined volume of standard gas (e.g. H₂S or ethanethiol) generated in a Tedlar bag was added to each reactor through the Mininert valve. H₂S standards were generated from 1.99 or 5% H₂S standard tanks. Ethanethiol, DMS, and DMDS standards were generated using neat liquids and added as defined pure liquid volumes to a defined volume of N₂ gas or air in a Tedlar bag and allowed to evaporate. If the volume of gas added was greater than 0.3% of the headspace volume, the volume of gas to be injected was removed from the headspace via a gas-tight syringe to prevent dilution effects. In the reactor systems used to measure the adsorption capacity, headspace concentrations were measured after static incubation at 30 °C for 24 h, slurry systems were shaken at 250 rpm at 30 °C for 24 h. In systems used to measure adsorption/reaction rates, after compound injection into the reactor headspace (via a gas-tight syringe), the Mininert valve was closed and the reactor briefly shaken. Before sampling, the reactor was allowed to stand for 1 min at room temperature. Subsequently, the headspace was sampled 10–20 times using a gas-tight syringe (100 µl) and the compound concentration (or peak area) determined by GC or GC/MS analysis. Compounds were spiked into the headspace multiple times and the adsorption/reaction monitored with time.

2.5. Continuous flow studies

The extent of H₂S conversion was measured in a continuous flow packed bed reactor (2.54 cm i.d., 30.48 cm length, kimax column). Compressed air or N₂ (1 l/min) was mixed with H₂S (5% in N₂) using a mass flow controller and passed through the column. SCR ash (10 g dry ash + 3.33 g H₂O) was distributed in glass wool and packed throughout the reactor. Tees (stainless steel, Swage-Lock) with septum were installed at the inlet and outlet of the column for sampling. All tubing was 6.35 mm i.d. Teflon and fittings were constructed of stainless steel (Swage-Lock) and each end of the column contained a threaded teflon plug for an air-tight fit.

Portable GC/MS units were used to measure H₂S levels in the inlet and outlet of the packed bed reactor (HAPSITE Inficon, East Syracuse, NY). Gas samples were analyzed under isothermal conditions (80 °C) using an SPB-1 sulfur column (Supelco, Bellefonte PA). Columns were standard 30 m capillary columns (0.32 µm i.d. × 1 µm film) spun into small cartridges, with 5 m of pre-column separated from the main column by a tee. Injection volume was controlled by a sample loop volume and injection time (1–10 s). Gas samples were sampled directly from tees at the inlet and outlet of the column using a heated probe (50 °C) and a defined flow rate of 145 ml/min for approximately 0.5–1 min. Nitrogen was used as the carrier gas in the GC/MS system (3.5–3.7 ml/min).

The mass spectrometer consisted of an ionizer (70 eV), a mass selector (1–300 amu), and an ion detector (scan rate 1000 amu/s @ 10 points per amu). Two internal standards, 1,3,5-tris(trifluoromethyl)benzene (100 ppmv) and bromopentafluorobenzene (50 ppmv), were used to tune the MS and injected with each gas sample. A non-evaporable getter pump (NEG) was used to generate the required vacuum, which necessitated the use of nitrogen as the carrier gas. The mass spectrometry (MS) detector was tuned before each analysis or every 8 h. Selective ion monitoring (SIM) was used to improve sensitivity in the H₂S analysis. In the SIM mode mass/charge ratios (*m/z*) of 33, 34, 69, and 117 (internal standard) were selectively scanned instead of a range. Standard curves and continuous flow studies were based on the measured peak area of *m/z* 34.

3. Results

Hydrogen sulfide adsorption was measured in batch reactors using two different amounts of coal fly ash (0.1 and 1.0 g) and by varying the initial gas phase concentration from 10 to 500 ppmv (0.01–0.7 g/m³). The adsorption capacity of the SCR (ash determined by a mass balance) for H₂S increased linearly with the initial gas phase concentration. In the reactors that received 1 g of ash equilibrium H₂S concentrations were at or below detection limits indicating the capacity of the ash had not been exceeded. This result was observed when a smaller amount (0.1 g) of ash resulted in similar equilibrium gas phase concentrations and suggested a reaction may be responsible for H₂S removal (1000 mg/kg at 0.7 g/m³). Subsequently, batch reactor systems were repeatedly pulsed with H₂S to determine if the systems could be saturated, which would indicate adsorption as the removal mechanism. Hydrogen sulfide was consistently removed to below 2 ppmv (0.0043 g/m³) when repeatedly contacted with SCR ash (Fig. 1), suggesting that the ash catalytically oxidized the H₂S.

In addition, the structure of the compounds tested apparently, altered the adsorption/reaction results. DMDS had a much lower adsorption capacity for the SCR ash and the adsorption capacity did not increase with the initial gas concentration (maximum of 80 mg/kg). Moreover, after an initial decline, DMDS and DMS headspace concentrations remained constant in the batch reactor systems (data not shown). Contrary to DMDS and DMS, the addition of ethanethiol to coal fly ash resulted in the rapid loss of ethanethiol and the formation of diethyl disulfide (Fig. 2).

3.1. Effect of water

As noted in the literature, the presence of H₂O potentially enhances H₂S oxidation [7,16] and thus the effect of moisture content on the adsorption/oxidation reaction was studied. Batch adsorption/reaction studies were performed with dry, 25% moisture, and completely

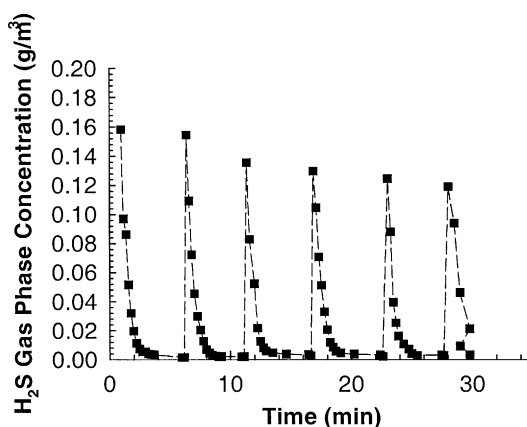


Fig. 1. The adsorption/reaction of H₂S. (■) at an initial gas phase concentration of 0.16 g/m³ (104.3 ppmv) with coal fly ash (1 g) from a selective catalytic reduction process under dry conditions and statically incubated at 23–25 °C. The batch reactors were periodically spiked and the adsorption/reaction measured with respect to time.

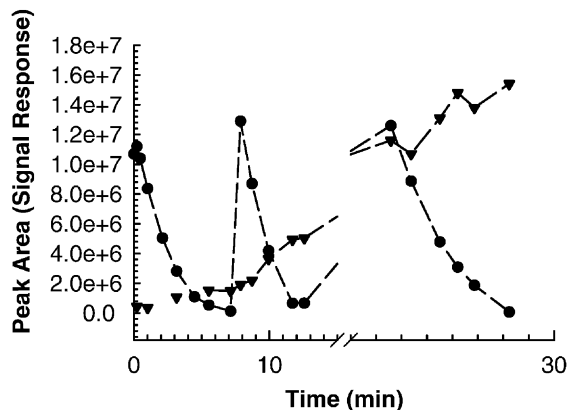


Fig. 2. The adsorption/reaction of ethanethiol. (●) with coal fly ash (1 g) from a selective catalytic reduction process under dry conditions and statically incubated at 23–25 °C and subsequent formation of diethyl disulfide; (▼) identified via GC/MS analysis.

saturated SCR ash. Initial rate data indicated that the presence of water increased the rate of H_2S and ethanethiol loss (most notably for ethanethiol) from the headspace of the batch reactors (Fig. 3).

3.2. Mixtures of sulfur compounds

Previous research indicated that DMS (CH_3SCH_3), DMDS (CH_3SSCH_3) or MT (CH_3SH) could only be oxidized by activated carbon in the presence of H_2S [9,10]. Given the fact that

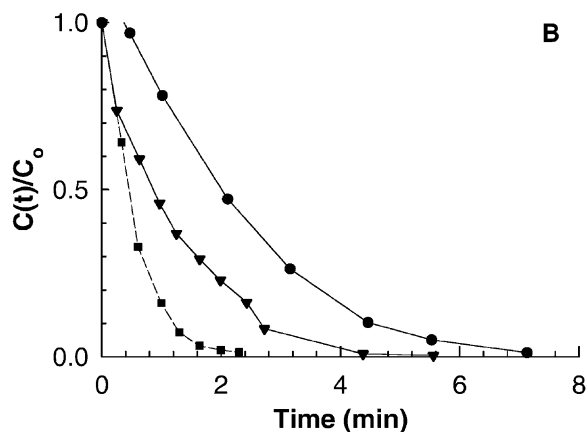


Fig. 3. The effect of water addition on the adsorption/reaction of ethanethiol with coal fly ash (1 g) from a selective catalytic reduction process at 23–25 °C. (●) Dry ash; (▼) 25%, w/w moisture; (■) slurry (1 g in 10 ml H_2O). The fractional decline in ethanethiol is shown vs. the change in time after injection of the reactant. It should be noted that the data is based on peak area only.

individually DMS and DMDS were not catalytically oxidized by coal fly ash, mixtures of DMS or DMDS and H_2S were tested. Contrary to previous work with activated carbon, the addition of H_2S to DMS or DMDS did not result in a measured loss of the two compounds in the batch reactor systems; H_2S was rapidly removed but not DMS or DMDS (data not shown). Results were similar for systems that received H_2O as well.

3.3. Continuous flow experiments

Initial results indicate that a stream containing an inlet H_2S concentration of 400–500 ppmv was reduced to 200 ppmv at a 4.6 s residence time (based on the packing height of the ash). The removal efficiency remained at 50% for approximately 4.6 h or 3500 reactor volumes (Fig. 4). To determine if O_2 is required for the reaction to take place and confirm that coal fly ash catalyzed H_2S oxidation, air was replaced with nitrogen. Although, there

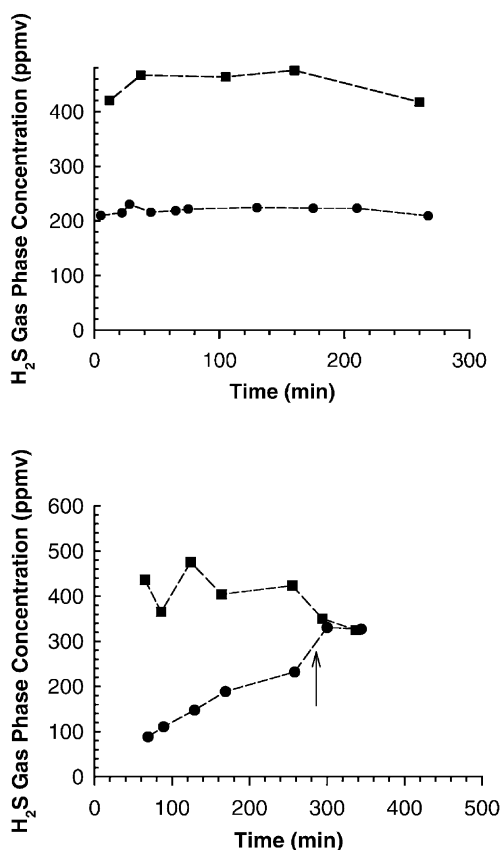


Fig. 4. Continuous conversion of a gaseous H_2S stream using a reactor packed with 10 g of coal fly ash (25% moisture) at 23–25 °C and the effect of switching from air to nitrogen (arrow) on the continuous conversion of a gaseous H_2S stream. (■) Inlet H_2S ; (●) outlet H_2S .

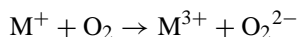
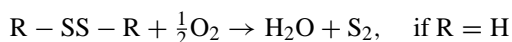
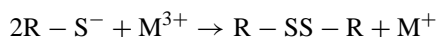
was a variation in the inlet H₂S concentration, the inlet and outlet H₂S concentrations rapidly equalized, indicating the reaction does not take place without oxygen (Fig. 4). Additional continuous flow studies using N₂ as the carrier gas resulted in complete lack of H₂S removal (data not shown).

4. Discussion

The results indicate that H₂S and ethanethiol were catalytically oxidized in the presence of coal fly ash (ash from a process using selective catalytic reduction for NO_x removal). In batch reactors that contained H₂S or ethanethiol (CH₃CH₂SH) without SCR ash, equilibrium concentration or peak areas remained constant. DMS (CH₃SCH₃) and DMDS (CH₃SSCH₃) did not react with the ash since equilibrium concentrations remained constant in the batch reactor systems. Moreover, ethanethiol oxidation resulted in the formation of diethyl disulfide (CH₃CH₂SSCH₂CH₃). These results are similar to Dalai et al. (1997) [17] who reported the formation of CH₃SSCH₃ from CH₃SH using activated carbon. The fact that H₂S and CH₃CH₂SH were oxidized, when CH₃SCH₃ and CH₃SSCH₃ were not, indicate that the sulfur atom is the site of the reaction and must be free for interaction with an active site on the SCR ash (i.e. under the conditions studied).

4.1. Potential mechanism(s)

Several different mechanisms for H₂S oxidation have been proposed and could be responsible for the catalytic oxidation of H₂S and CH₃SH (similar to ethanethiol). The fact that water addition increased the rate of oxidation suggests that H₂O along with O₂ is a required reactant and that the reaction takes place within the water phase condensed on the surface of the ash or in the pores. The data suggest that both H₂S (or other reduced sulfur compounds) and oxygen must be transferred from the gas phase to the liquid phase coating the surface of the fly ash. Once in the liquid phase, diffusion coupled with chemical reaction may occur in this liquid film or the reactants may diffuse through the liquid film and adsorb at the surface of the ash where a surface reaction could take place. Previous research suggested a mechanism involving transition metal ions and could account for both H₂S and ethanethiol oxidation [16]. In the suggested mechanism, R could be H, CH₃, or CH₃CH₂ groups. We believe that if the R group is CH₃ or CH₃CH₂, oxygen is not capable of reacting with R–SS–R or R–S–R and thus no further reaction occurs beyond this point, which accounts for the formation of diethyl disulfide from the ethanethiol.



Coal ash is reported to have high concentrations of metal oxides, such as Al₂O₃ (14–20%, w/w), Fe₂O₃ (8–14%, w/w), and TiO₂ (1–1.6%, w/w) that could act as catalysts [13]. The ash

used in these experiments had an iron, aluminum, nickel, and vanadium content of 19600.0, 6926.0, 21.7, and 40.0 ppm, respectively with little carbon (7.6%) and a small surface area compared to activated carbon ($7.7 \text{ m}^2/\text{g}$). Iron oxide catalysts are used to catalyze the oxidation of H_2S [18] and other metals have been added to activated carbon to alter catalytic selectivity [19].

5. Conclusions

Experimental results suggest that coal fly ash from a selective catalytic reduction (SCR) process promoted the catalytic oxidation of H_2S and ethanethiol at room temperature (23–25 °C). The most conclusive set of data were the results demonstrating the formation of diethyl disulfide from ethanethiol in the presence of SCR ash. It is likely that the metal oxides present in the SCR ash were responsible for oxidation of the reduced sulfur compounds. Future research will focus on: (i) the kinetics and decay of H_2S oxidation using coal fly ash, (ii) methods to enhance the oxidation of other reduced sulfur compounds (e.g. ethanethiol), (iii) development of catalyst pellets to reduce pressure drop, and (iv) methods to better understand the mechanism and regenerate the catalyst. These experiments will provide a basis for catalyst and reactor design to remove reduced sulfur compounds from agricultural, solid waste, and chemical industry emissions using coal fly ash.

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