DE-FG22-91PC91306

"Sorption and Chemical Transformation of PAHs on Coal Fly Ash"

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The objective of this research is to characterize the interactions of coal fly ash with polycyclic aromatic hydrocarbons (PAHs) and their derivatives, and to understand the influence of the surface properties of coal ash (and other atmospheric particles) on the chemical transformations of polycyclic aromatic compounds. Studies to be carried out in this project include:

(a) Fractionation of heterogeneous coal fly ash samples into different particle types varying in size and chemical composition (carbonaceous, mineral-magnetic, and mineral nonmagnetic);

(b) Measurement of the rates of chemical transformation of PAHs and PAH derivatives (especially nitro-PAHs) and the manner in which the rates of such processes are influenced by the chemical and physical properties of coal fly ash particles;

(c) Chromatographic and spectroscopic studies of the nature of the interactions of coal fly ash particles with PAHs and PAH derivatives;

(d) Characterization of the fractal nature of fly ash particles (via surface area measurements) and the relationships of "surface roughness" of fly ash particles to the chemical behavior of PAHs sorbed on coal ash particles;

(e) Identification of the major products of chemical transformation of PAHs on coal ash particles, and examination of any effects that may exist of the nature of the coal ash surface on the identities of PAH transformation products; and

(f) Studies of the influence of other sorbed species on the chemical behavior of PAHs and PAH derivatives on fly ash surfaces.

PAHs are deposited, under controlled laboratory conditions, onto coal ash surfaces from the vapor phase, in order to mimic the processes by which PAHs are deposited onto particulate matter in the atmosphere.

Much of the work performed since the inception of the current grant has involved preparation of apparatus and techniques for these investigations, as well as initial feasibility studies. Work performed, and results obtained, since the inception of the current grant is summarized below.

(1) The photochemical transformation of benz[a]anthracene (BaA) on model adsorbents (alumina, silica gel, graphitic carbon) has been studied. It is found that the major phototransformation product of BaA is benz[a]anthracene-7,12-dione (BaAD); the structures of BaA and BaAD are shown on the following page.

benz[a]anthrenene (BaA)

benz[a]anthracene-7,12-dione (BaAD)

BaAD, the photoproduct of BaA, is itself photosensitive and, upon illumination, undergoes photodecomposition to form products that as yet are unidentified.

The relative photoreactivities of BaA and BaAD appear to depend strongly on the nature of the sorbent surface. For example, on silica gel, the first-order rate constant for phototransformation of BaA is 100 times greater than that for BaAD. However, on a nonmagnetic mineral fraction of a Texas lignite ash, the first-order rate constant for photodecomposition of BaA exceeds that for BaAD only by a factor of 2. (Both compounds exhibit much more rapid phototransformation when sorbed on silica gel than on the lignite ash fraction, but the difference between the photodecomposition rates on the two sorbents is much greater for BaAD than for BaA.) The strong sorbent-surface effect on the relative phototransformation rates of BaA and its oxygenated photoproduct is extremely interesting and potentially significant. Hence, this issue will receive considerable emphasis in future work.

(2) The feasibility of measuring heats of adsorption for PAHs on fly ashes by gas-solid chromatography has been studied. In such a measurement, a gas chromatography (GC) column is packed with the adsorbent of interest, and is inserted into a conventional gas chromatograph. A solution of the PAH of interest is injected onto the column (the solvent is intercepted by a molecular sieve precolumn, so that only the PAH vapor actually reaches the GC column). The retention parameters and shape of the GC peak for the PAH is measured as a function of temperature; using a technique called "elution by characteristic point" (see Reference [1] for details), the heat of adsorption of the PAH can be calculated from the GC data if certain assumptions are valid.

A key assumption that must be made is that the rate at which the PAH in question adsorbs onto, and desorbs from, the particulate surface of interest is very rapid. For the case of pyrene as the PAH, and various coal ashes and ash fractions as adsorbents, our data indicate that this assumption is not always valid. Therefore, the use of GC methods for evaluation of heats of adsorption of PAHs containing ≥ 4 rings on coal ashes does not appear generally feasible, though it may be possible in the case of certain coal ashes that are relatively low in carbon content and have relatively "smooth" surfaces characterized by relatively few pores. It appears that acquisition of valid heats of adsorption for ≥ 4 -ring PAHs via GC would be feasible only at column temperatures substantially higher than the maximum operating temperatures of commercial GC apparatus.

A more encouraging set of preliminary results has been obtained by using toluene, rather than pyrene, as the adsorbate molecule. Toluene is much more volatile than pyrene, and it appears that rates of adsorption and desorption of pyrene on coal ashes are rapid at temperatures accessible with conventional gas

chromatographs. While toluene is of course not a PAH, its use in these experiments will enable us to compare the affinities of various coal ashes, and ash subfractions, for aromatic hydrocarbons. Such data would ultimately enable comparisons of the affinities of fly ash surfaces for aromatic hydrocarbons with the effects of the fly ash surfaces on the phototransformation rates of sorbed PAHs to be carried out. Thus, the use of toluene (and perhaps benzene and naphthalene) as "probe solutes" for evaluating the relative affinities of fly ash surfaces for aromatic compounds, by GC using the technique of elution by characteristic point, will be extended.

(3) A large quantity of a well-characterized coal stack ash has been obtained from the Oak Ridge National Laboratory (Analytical Chemistry Division), and fractionation of this material according to size and chemical composition is currently being performed, using techniques previously developed in this laboratory [2]. This ash, when fractionated, will be used in continuing efforts to understand how differences in particle composition and size influence the photochemical transformation of sorbed PAHs.

(4) PAHs are much less susceptible to photochemical transformation when sorbed on coal fly ash than when sorbed on most other types of particulate matter [3]. One plausible explanation of this fact is that coal ash particles (especially carbonaceous particles) are porous and dark in color. Thus, it is possible for sorbed PAH molecules to penetrate into pores and thus be "shielded" from the incident light. While this argument is highly plausible, there is presently no direct evidence to indicate its validity.

If the above argument is valid, coal fly ash surfaces should tend to exhibit fractal properties [4] (fractal surfaces are "self-similar"; that is, they do not appear to change in a major way in shape when viewed at different levels of magnification). Numerous particulate materials, including various soils, carbon blacks, and coal dusts, have been shown to exhibit fractal characteristics [5].

The fractal characteristics of a solid can be examined by measuring the surface area as a function of particle diameter or (more definitively) size of the adsorbate molecule. If a surface exhibits fractal characteristics, the surface area available to a small adsorbate molecule is significantly greater than that available to a large adsorbate molecule (because the small adsorbate can penetrate pores that are inaccessible to the larger adsorbate).

Preliminary measurements, based on surface areas as measured using a single adsorbate (nitrogen) on coal ash samples and fractions of varying particle size are consistent with the presumption that the coal ashes that were studied exhibit fractal characteristics. To render this tentative conclusion more definitive, similar measurements must be performed using other adsorbate molecules of different molecular size. Those measurements are in progress.

(5) Apparatus and techniques are under development for the deposition of nitro-substituted PAHs on coal ash samples, in order that their transformations on different ashes can be studied. The first nitro-PAH to be studied is 1-nitropyrene.

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