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"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. Currently active studies 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;

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.

Progress in the previous three-month period (May 1 - July 31, 1992) is summarized below.

(1) A summer faculty research participant (Dr. David A. Franz, Lycoming College, Williamsport, PA) and an undergraduate research student (David Patterson) have carried out preliminary measurements of adsorption isotherms and heats of adsorption for toluene on various model adsorbents and coal fly ash fractions, using gas-solid chromatography. In these measurements, gas chromatographic columns are packed with the fly ash (or other particulate solid) to be studied, a suitable "probe solute" is injected onto the column, and the chromatographic retention behavior of that probe solute is measured as a function of temperature and quantity of probe solute injected onto the column [1]. We are using toluene, rather than a PAH, as "probe solute" because toluene is a liquid at room temperature and therefore does not have to be dissolved in a liquid solvent prior to injection onto the gas chromatographic column. Previous studies in this laboratory have shown that, when liquid solutions of pyrene are injected onto columns of fly ash, the solvent

sometimes perturbs the retention behavior of pyrene, presumably by modifying the surface in some unknown manner [2]. This problem is avoided by use of toluene as the probe solute.

The results obtained to date indicate that toluene is a useful "probe solute" for measuring the relative affinities of various fly ash fractions for aromatic solutes. In general, the adsorption isotherms obtained for toluene on fly ash fractions can be fit to a Freundlich [3] adsorption isotherm equation, which implies that the adsorbent surface in question is heterogeneous. For most fly ash fractions studied thus far, the measured heat of adsorption decreases as the quantity of toluene injected onto the column increases. This observation also indicates that the fly ash surfaces are heterogeneous. For a homogeneous (or nearly homogeneous) surface, virtually all adsorption "sites" for a particular solute exhibit approximately the same affinity for the solute; hence, the measured heat of adsorption is virtually independent of the amount of solute that is brought into contact with the surface. However, when the surface is heterogeneous, the measured heat of adsorption decreases as the amount of solute is increased; this variation can be used to make inferences regarding surface site energy distributions if certain assumptions and approximations are made [4].

Data obtained to date are summarized below.

Adsorbent	Surface area, m^2/g	% Carbon[a]	q[b]	ΔH, kJ/mol
Fractosil 1000[c]	11.6	-		41
Texas lignite fly ash, non-magnetic fraction, 75-124 μm particle size	2.7	0.60	1.1	37
Kaneb[d] coal fly ash, heavy non-magnetic mineral fraction, 75-124 μm particles	1.7	nd[e]	1.2	8
Kaneb coal fly ash, light non-magnetic mineral fraction, 75-124 μm particles	1.6	nd[e]	1.3	18
Kaneb coal fly ash, carbonaceous fraction, 75-124 μm particles	25.5	67.3	0.8	62
Kaneb coal fly ash, magnetic fraction, 45-74 μm particles	0.75	0.32	1.2	16

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[a] Weight percentage of elemental carbon present in the adsorbent.

[b] Quantity of toluene injected, in μmoles/m^2 of surface.

[c] A silica gel having a relatively homogeneous surface, used as a model adsorbent.

[d] A bituminous coal fly ash relatively high in carbon (unfractionated ash is 5.5 %C [5].

[e] Not determined, but expected to be 2% or less.

On the basis of the data obtained to date, it is clear that the affinity for toluene of the various types of fly ash particles differs dramatically (heats of adsorption ranging from 62 kJ/mol for the highly carbonaceous fraction of the bituminous coal fly ash to 8 kJ/mol for a nonmagnetic mineral fraction of the same fly ash). The results obtained to date suggest that use of toluene as a "probe solute" in studies of this type should be continued and expanded to other fly ashes and ash fractions. The use of nitrobenzene and pyridine as "probe solutes" also will be examined, because studies of the phototransformation of nitro and nitrogen heterocyclic derivatives of PAHs on various fly ashes will represent a significant emphasis in this work.

(2) Separation into compositional subfractions of the "Kaneb" bituminous coal fly ash (see above) has been completed; microanalytical data (weight percentages of carbon) for many of these fractions have not yet been obtained.

(3) Measurements of surface areas of coal fly ash subfractions, to enable the fractal properties of the particles to be determined, are continuing.

(4) Apparatus to study the interactions of PAHs sorbed on coal fly ash with hydroxyl (OH) radicals is being assembled. In the atmosphere, OH radicals are produced by photochemical reactions involving such species as ozone, hydrogen peroxide, and nitrous acid. PAHs in the gas phase react rapidly with OH, and this is thought to be the dominant mode for chemical transformation of gas-phase PAHs in the atmosphere (e.g., 2-4 ring PAHs that have appreciable vapor pressures at room temperature and may thus be present in the atmosphere at least partially in the gas phase) [6]. Reactions of gas-phase PAHs with OH in the presence of NO_2 are thought to be a major route for atmospheric production of mutagenic nitro derivatives of PAHs [6]. The question as to whether particulate-phase PAHs are similarly reactive with OH has not been addressed. We are in the process of initiating such a study.

Our apparatus for these studies generates OH radicals by reaction of H atoms with NO_2:

$$H + NO_2 \rightarrow OH + NO$$

THe hydrogen atoms are formed via a microwave discharge in a dilute stream of H_2 and NO_2 in helium. Care must be exercised to remove nitric acid, a common contaminant in cylinder NO_2. The resulting gas stream containing OH radicals is passed through a chamber containing a PAH sorbed on fly ash; other gases can be added to the gas stream as needed. Construction of the apparatus has been completed; the only remaining task that must be completed before experiments with adsorbed PAHs commence is development of a reliable method for detecting and quantifying the OH radical concentrations in the gas stream.

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