FULLERENIC CARBON IN COMBUSTION GENERATED SOOT

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Introduction

The interest in fullerenes has expanded from C60, C70 and other now well known molecules to larger structures including giant fullerene molecules Cn with n≥100, nanotubes and nanoparticles, all comprised of curved sheets of 5-, 6-, and in some cases 7-membered rings versus planar sheets of 6-membered rings as in graphite. While these larger structures are usually produced in the same types of carbon vaporization systems as used for C60 and C70 synthesis, they can also be produced in flames [1, 2] as can C60 and C70 [3, 4]. Whether curved fullerene carbon might also be present in flame-generated particles is addressed here.

Experimental

Plug-flow laminar flames of acetylene, benzene or ethylene premixed with oxygen and an inert diluent were stabilized on a 7 cm diameter burner in a low-pressure chamber. Samples of soot and other condensable species were collected from within the flame using a water-cooled probe and filter, and from a water-cooled surface contacting the tail of the flame. Flame conditions were varied over the ranges: pressure, 20-97 torr; C/O atomic ratio, 1.06 (C2H2), 0.86-1.00 (C6H6) or 1.07 (C2H4), feed gas velocity (298 K), 25-50 cm/s; and diluent concentration, 0-44%. The peak temperature in the different flames was 1930-2050 K.

A second combustor consisted of a 250 cm³ jet-stirred reactor coupled to a downstream 5 cm i.d x 30.5 cm long plug-flow reactor, from the exit of which samples of soot and condensibles were collected using a water-cooled suction probe and filter. Premixed ethylene and air with a C/O atomic ratio of 0.73 was burned under conventional conditions of atmospheric pressure, turbulent flow, and temperature and resident time of 1700 K and 20 ms.

The samples were analyzed in a TOPCON 002B high resolution transmission electronic microscope (HRTEM) operated at 200 keV with a point resolution of 0.17 nm, a spherical aberration coefficient of 0.4 nm, and exposure times below the minimum for electron beam damage. A small portion of each sample was dispersed in toluene using mild sonication at room temperature for 20 min. Drops of suspension, including toluene extract and insoluble material, were placed on holey carbon films on electron microscope grids and dried under vacuum, thus depositing all the sample material for HRTEM analysis.

Results and Discussion

Fullerenes C60, C70 and larger structures including giant fullerenes, nanotubes and nanoparticles were found in varying amounts in the low pressure benzene and acetylene flames [1, 2] but were not detected in the conventional atmospheric pressure combustion of ethylene. HRTEM images (Fig. 1) of the internal structure of the soot particles reveals the presence of continuous, smoothly curving layers or shells, i.e., fullerene carbon, as distinct from flat graphite carbon. The shells, mostly incompletely closed, occur alone or aligned concentrically in varying numbers, and are more prominent in soot from the fullerene forming flames although they are a significant part of the structure of the conventional combustion soot which also contains flat layers oriented randomly or aligned either parallel in stacks or as segments of quasi shells. The distinction between smooth continuous fullerene shells and graphic quasi shells is based on comparison with the continuous shells observed in nested nanotube caps and onions from fullerene forming flames. The fraction of the internal structure of the soot represented by curved layers varies from almost 100% in some of the fullerene-forming flames to as large as 50%, with many of the shells subtending smaller angles, in the conventional combustion soot.

The prevalence of curved layers in flame soot is of interest with regard to mechanisms of soot formation. Polycyclic aromatic hydrocarbons (PAH) are probably reactants in soot nucleation and growth [12], and many of the PAH in flames contain five-membered rings (5-rings) [13]. PAH with 5-rings surrounded by 6-rings are curved, and one such PAH has been detected in flames [14]. The presence of curved layers in soot prior to condensed phase intermolecular rearrangement (tempering or carbonization) would be consistent with curved PAH serving as soot nucleation and growth reactants.

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Conclusions

Curved layers or shells indicative of fullerene carbon are prevalent in soots from the fullerene forming and conventional flames studied here. This observation greatly extends the range of conditions under which curved carbon is known to prevail, from the previously known highly energetic vaporization [5-10] or electron irradiation [11] of carbon to the thermally milder conditions of hydrocarbon combustion. Structural features such as the content of fullerene carbon relative to graphitic carbon and the degree of closure, mutual alignment and other characteristics of the shells in flame soots vary with flame conditions and thus may be controllable. If certain combinations of these features are found to offer novel properties of practical interest, the material could be produced in large quantity with scaled-up combustion equipment.

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References


Figure 1. HRTEM image of internal structure of soot from a fullerene-forming benzene oxygen flame.