Ultrafine Particles from Combustion Systems

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The processes by which carbonaceous nanoparticles are produced from combustion of liquid and gaseous fuels are reviewed. The focus of the talk is on the formation and properties of nanoparticles in laboratory laminar, premixed and diffusion flames and on the most popular methods of sampling and detection of these particles. Particle chemical nature is analyzed from data obtained by several measurement techniques. Measurements characterizing nanoparticles in the exhausts of practical combustion systems such as engines and commercial burners are also reported.
Combustion of fossil fuels produces carbonaceous nanoparticles both in premixed and non-premixed flame conditions. Two classes of carbonaceous material are mainly formed in combustion: nanoparticles with sizes in the range 1-5nm, and soot particles, with sizes from 10nm to 100nm. Chemical and spectroscopic analysis give an indication of the chemical nature of the particles and show that the smaller particles can be thought as staked PAH structures or polymer-like structures containing sub-units with aliphatic and aromatic bonds and occasionally oxygen, depending on the flame environment.
A simple modelling analysis is used to show how the growth of aromatics and the chemical nature of the particles depend on temperature and radical concentration distributions encountered in flames.
Staked PAH structures are formed if physical molecular growth mechanism, based on PAH dimerization, is favored by low temperatures and low radical concentrations. On the other hand, aromatic-aliphatic linked structures are formed when chemical-growth mechanism is enhanced, i.e. higher temperatures and higher radical concentrations. Oxidative-pyrolytic conditions, typical of fuel-rich, premixed flames, favor the latter mechanism while purely-pyrolytic conditions, typical of the fuel side of diffusion flames, favor the aromatic dimerization.
The process of soot formation is the coagulation of the 1-5 nm particles, which at the same time add compounds from the gas-phase and lose H, gaining a higher condensed-ring aromatic or graphitic structure.
Nanoparticles are also found in the exhaust of practical combustion systems. This has been mainly attributed to condensation of low volatility hydrocarbons during dilution and cooling of the exhausts. However, the similarity of the chemical properties and the size distribution functions of the emitted particles with those found in laboratory flames suggests that combustion-formed nanoparticles can escape the combustion process and be emitted into the atmosphere. Thus combustion, as well as the fuel, may have a dominant role in determining the type and amount of particles emitted.
Nanoparticles are present in low mass concentration, but surprisingly high number concentrations due to their very low sizes. The emission of these particles into the

atmosphere constitutes a serious concern for health and for their contribution to photochemical smog. The smallest particles play a particularly important role in health since they are able to penetrate deeper than larger particles into the respiratory system. They may also affect the radiation balance of the atmosphere by serving as condensation nuclei for cloud formation and for contrails in the upper atmosphere. For these reasons, the role of combustion-formed nanoparticles is of central interest in the field of atmospheric chemistry. These particles may account for a large part of the organic carbon in urban atmospheres and they might also explain the phenomenon of “nucleation burst” after agglomeration in rain.

Nanoparticles have low coagulation rates at flame temperatures. This interesting behavior may explain why they escape exhaust systems without significant growth at high temperature. The low coagulation rate is due to the weak van der Waals-interactions between particles relative to their thermal energy and it may also be related to the chemical nature of the particles. The presence of functional groups containing oxygen within the chemical structure of nanoparticles can decrease their polarizability reducing the strength of van der Waals-interactions. If oxygen containing functionalities are present in combustion-generated nanoparticles, it is also possible to explain why nanoparticles with sizes below 3nm remain dispersed in water samples in contrast to larger and more graphitic soot particles. The presence of oxygen in nanoparticles is of great importance and it may also play a role in how these particles affect biological systems.

The low coagulation rate of nanoparticles means that some of them survive for a long time. They undergo atmospheric reactions and they can also spread to areas without particle emissions making nanoparticles emitted from combustion systems a global problem.