Removal of very small submicronic particles by Water Nucleation: Effects of Particles Chemical-Physical Properties

Mariarosaria de Joannon, Michela Alfè*,*
Gennaro Cozzolino, Valentina Gargiulo*, Pino Sabia*, Raffaele Ragucci**

**** Istituto di Ricerche sulla Combustione - C.N.R., Napoli – Italy***

Supporting information

SI.1 Supporting theory on homogeneous and heterogeneous droplet nucleation and growth

The classical homogeneous nucleation theory, modified by Fletcher [1] for heterogeneous condensation on spherical, homogeneous particles is often used in the literature in the evaluation of the nucleation rate. In this case the evaluation of the saturation vapor pressure takes into account the interaction between the solid nucleus and the condensing species by adding the dependence of P°(T) on the contact angle through the parameter m as follows:

$$P(d) = P^{o}(T)\exp\left[\frac{1}{RT\rho_l}\sqrt{\frac{8\pi M_l^2\sigma_{lv}^3}{3k_B T\ln\left(4\pi R_p^2 K\right)}}f(m,x)\right] \qquad (s1)$$

where f(m,x) is a function of the size, the shape and characteristics of the solid particles

The Fletcher equation, does not take into account the microstructure of the particle, related to the surface roughness. Particles are often aggregations of primary particles of lower dimension and size. Thus, particle morphology and microstructure strongly affect the property of its surface. For instance, in the case of the carbonaceous particles generated using graphite electrodes used in the present work, each particle is an aggregate of primary particles in the size range between 3-5 nm: its final shape will be very irregular (not spherical) and a fractal dimension may be evaluated for its surface [2]. As a consequence, the particle surface is dotted by nanometric cracks and pores, where the capillary condensation process could occur. On such a type of nano-structured surface the formation of liquid meniscus can be stabilized at under-saturation conditions with respect to the vapor bulk phase. It is possible to evaluate the equilibrium vapor concentration on such a surface structure by considering the formation of a liquid meniscus in the primary interparticle cavities by means of the following expression:

$$P_H = P_o e^{\left(\frac{M_w \sigma_{lv}}{\rho_l RT} H\right)} \quad (s2)$$

where P_o is the equilibrium vapor pressure on a flat surface (i.e. P°(T)) and P_H is the equilibrium vapor pressure on a surface with negative curvature $H = \frac{1}{2} r_k < 0$, where r_k is the Kelvin radius, defined as [3]

$$r_k = \frac{2\sigma_{lv}}{n_l k_B T \log(p/p_s)}$$

where k_B is the Boltzmann's constant.

This process has a very low characteristic time on the order of water vapor molecules transition time on the particle surface, $\tau_o = 10^{-16}$s, [4] so it appears to be the fastest process occurring in series during the formation and growth of a droplet on a particle substrate. It is worth to note that the saturation value of vapor concentration $X_{v,\,sat}(H)$, evaluated from P_H, strongly depends on surface morphology, chemical and physical properties (surface tension of vapor liquid interface, contact angle between solid and liquid phase) of both particles and condensing vapor species that rigorously should be evaluated according to nano-thermodynamic or fluctuation theory. Such an approach goes beyond the aims of this work. For our purpose $X_{v,\,sat}(H)$ was evaluated as a function of macroscopic physical properties of phases involved in the formation and growth process of droplets on particle surfaces. Thus, it represents a useful tool (albeit a non-rigorous approach) for the interpretation of experimental results carried out from polarization ratio measurements.

The evaluation of surface roughness does not complete the list of properties that affect the values of saturation parameters. For instance, the presence of soluble species or functional groups on solid particles drastically changes the saturation point due to its interactions with condensing species. In the first case, the Köhler theory [5, 6] takes into account the activity of the condensing species for the evaluation of the saturation point. On the other hand, also functional groups present on internal and external particle surfaces strongly affect the condition under which the condensation takes place. For instance, functionalities containing either oxygen, nitrogen or sulfur seem to reduce the vapor concentration needed to reach the saturation conditions, which leads to a shift of surface properties from hydrophobic to hydrophilic behavior. Also in this case the expression for vapor pressure is modified adding a term that takes into account the interaction of condensing species with a functionalized substrate surface.

However, the expressions used in these cases increase the level of empiricism. In fact, the accommodation factors in such a formula have been obtained by fitting the experimental data and cannot be easily estimated by extrapolated under a specific set of conditions [5].

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SI.2 Refractive index of composite sphere

In this work the Bruggeman approsimation [7] was used to evaluate the refractive index of composite sphere formed by an adsorbing host sphere (graphite, iron and nickel) in a water droplet by varying the volume ratio of the inclusion. The results are summarized in the table si.1.

Volume ratio, f	C	Fe	Ni
1 (particle)	1,92 + i0,66	2,92 + i2,92	1,88 + i3,5
0,1	$1{,}33 + i3{,}67\cdot10^{-2}$	$1{,}54 + i1{,}04\cdot10^{-1}$	$1{,}53 + i1{,}73\cdot10^{-1}$
0,01	$1{,}33 + i6{,}07\cdot10^{-3}$	$1{,}35 + i6{,}33\cdot10^{-3}$	$1{,}36 + i7{,}87\cdot10^{-3}$
0,001	$1{,}33 + i6{,}66\cdot10^{-4}$	$1{,}33 + i6{,}024\cdot10^{-4}$	$1{,}33 + i7{,}29\cdot10^{-5}$
0,0001	$1{,}33 + i5{,}52\cdot10^{-5}$	$1{,}33 + i5{,}99\cdot10^{-5}$	$1{,}33 + i5{,}99\cdot10^{-5}$
0 (water)	1,33 +i0	1,33 +i0	1,33 +i0

Table si.1 : refraction index of composite sphere for the selected material by varying volume ratio

SI.3. Trend of polarization ratio of the C, Fe and Ni-based particles fed to the chamber as function of axial coordinate for Xv=0.

The trend of polarization ratio profiles showed in Fig. S.1 suggests that any phenomenon relative to particles size variation, such as coagulation, occurring among the graphite, iron and nickel particles can be neglected.

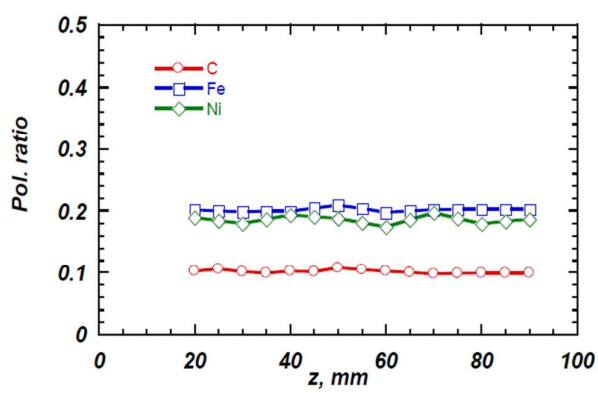

Figure S1: Polarization ratio of C, Fe, Ni – particles

Although the theoretical value of the polarization ratio should be equal to zero for particle light scattering described by the Rayleigh model, the experimental literature values of the ratio collected at 90° range between 0.01 and 0.1, due to the finite collecting angle of the diagnostic system. The γ values reported in Fig. S1 are also consistent with the calculated values after accounting for both the collection system characteristics and the generated particle properties and size distributions. In the case of iron and nickel particles the scattered light is influenced by the different optical properties of materials considered i.e. different refractive index.