

# Surface Composition and Reactive Oxygen Species (ROS) Generation: Evaluation of Health Risks of soot Nanoparticles.

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## Background / Objectives

### Background

- Micro- and nanoscopic imaging of soot indicate a turbostratic structure composed of concave/convex graphene sheets (50 – 625 Å<sup>2</sup>), corresponding to large polycyclic aromatic structures of 30-40 annellated benzene rings [1];
- Surface composition of soot nanoparticles (NP) depends on combustion conditions (temperature, pressure, fuel/oxidant ratio,...), resulting in different families of surface functional groups [2];
- These surface functional groups control the NP reactivity. Strongly reducing surface functions are related to the oxidative potential of soot toward dithiothreitol (DTT; a reducing compound) [3] and are thought to generate reactive oxygen species (ROS) through a heterogeneous catalytic process.

### Objectives

- To characterize the surface functional groups of a panel of carbonaceous NP originating from internal combustion engines and from synthetic industrial processes;
- To understand the reaction mechanism for ROS production in solution, when carbonaceous NP, DTT and dissolved oxygen are present and to evaluate the turnover of the proposed heterogeneous catalytic mechanism.

## Methods

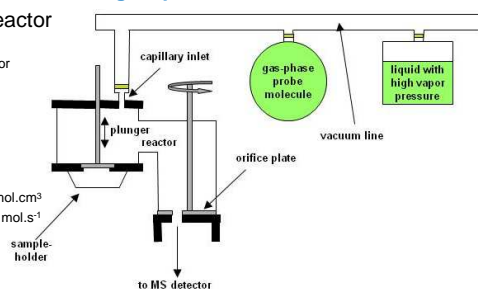
### Characterization of surface functional groups

- Use of a Knudsen flow reactor

Fig. 1: Schematic of a Knudsen flow reactor

#### Typical parameters of the reactor:

Volume: 1830 cm<sup>3</sup>  
 Estimated surface area: 1300 cm<sup>2</sup>  
 Sample surface area: 10 - 20 cm<sup>2</sup>  
 Escape orifice diameter: 1 mm  
 Typical concentration of probe gas : 10<sup>-13</sup> mol.cm<sup>-3</sup>  
 Typical molecular flow rate (probe): 5.10<sup>-14</sup> mol.s<sup>-1</sup>



- Use of reactive gas probes allowing the titration of surface functional groups

Fig. 2: Example of different gas probes considered in this work (red boxes)

#### Properties of probes:

O<sub>3</sub>: Strong oxidant in the gas phase.

Probing strong and weak reducing functions.

Ex: Olefins, certain polycyclic aromatic hydrocarbons,...

NO<sub>2</sub>: Weaker oxidant than O<sub>3</sub> in the gas phase.

Probing only strongly reducing functions.

Ex: Hydroquinones, phenol,...

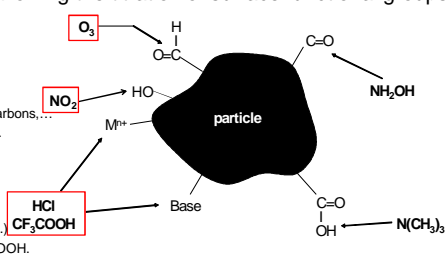
CF<sub>3</sub>COOH: Strong acid in the gas phase.

Probing strong and weak Lewis bases.

Ex: Basic oxides (α- or γ-pyrone, coumarines,...

HCl: Weaker acid in the gas phase than CF<sub>3</sub>COOH.

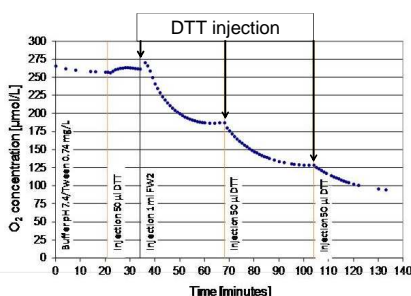
Probing only weak Lewis bases.



### Catalytic ROS production in presence of DTT, NP and dissolved O<sub>2</sub>

- Monitoring of O<sub>2</sub> consumption in a sealed reactor using a Clark electrode

Fig. 3: Typical response of the calibrated Clark O<sub>2</sub> electrode to a single addition of amorphous carbon suspension (FW2, 27 mg L<sup>-1</sup>) and three sequential albeit identical amounts of DTT (initial concentration of DTT in the reactor: 113 μM); pH: 7.4; Tween 80: 0.74 mg L<sup>-1</sup>, 25°C.



## Acknowledgments and References

MJR gratefully acknowledges the opportunity to participate in COST project CM 1404 SMARTCATS and thanks Profs. Urs Baltensperger and Alexander Wokaun of PSI for substantial support in the framework of the present investigations. JJS also thanks ANSES for partial funding.

[1] Müller et al., PCCP 2007, 9, 4016.

[3] Sauvain et al., Aerosol Sci Technol.2013, 47, 218.

[2] Setyan et al., ChemPhysChem 2010, 11, 3823. [4] Tapia et al., ES&T 2016, 50, 2946.

## Results / Discussion

### Surface functional groups of five carbonaceous NP's

- Figure 4 presents examples of uptake traces of NO<sub>2</sub> and O<sub>3</sub> for two carbonaceous NPs from internal combustion engines.

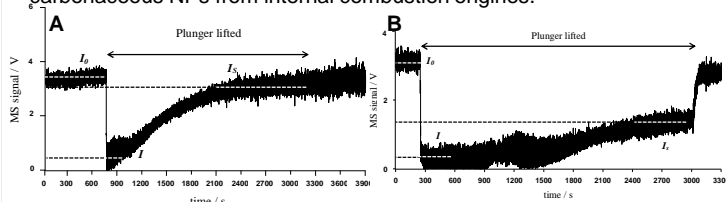


Fig. 4: A: Raw data of NO<sub>2</sub> uptake on 16.4 mg Diesel soot monitored at m/z 46, corresponding to an initial uptake coefficient γ<sub>0</sub> = 3.6.10<sup>-3</sup> [4]; B: Raw data of O<sub>3</sub> uptake on 10.97 mg Hydro-treated Vegetable Oil (HVO), monitored at m/z 48, corresponding to an initial uptake coefficient γ<sub>0</sub> = 4.4.10<sup>-3</sup> [4].

- Table 1: Results for reducing (O<sub>3</sub> and NO<sub>2</sub> probes) and basic surface functions (CF<sub>3</sub>COOH and HCl probes) on a panel of five NP's, expressed as a fraction of a molecular monolayer.

NP	BET [m <sup>2</sup> /g]	O <sub>3</sub>	NO <sub>2</sub>	CF <sub>3</sub> COOH	HCl
Number of molecules for one monolayer		7.4 × 10 <sup>14</sup>	7.1 × 10 <sup>14</sup>	4.0 × 10 <sup>14</sup>	8.6 × 10 <sup>14</sup>
Printex XE-2B	1000	1.2 × 10 <sup>-2</sup>	0.7 × 10 <sup>-2</sup>	1.4 × 10 <sup>-2</sup>	0.3 × 10 <sup>-2</sup>
GTS-6	6	steady-state reaction	0.5 × 10 <sup>-2</sup> steady-state reaction	3.8 × 10 <sup>-2</sup>	No reaction
GTS-80	80	0.5 × 10 <sup>-2</sup> steady-state reaction	0.6 × 10 <sup>-2</sup>	1.8 × 10 <sup>-2</sup>	1.5 × 10 <sup>-2</sup>
HVO	439	11.0 × 10 <sup>-2</sup>	11.0 × 10 <sup>-2</sup>	9.7 × 10 <sup>-2</sup>	0.8 × 10 <sup>-2</sup>
Diesel	333	33.0 × 10 <sup>-2</sup>	22.0 × 10 <sup>-2</sup>	7.0 × 10 <sup>-2</sup>	0.6 × 10 <sup>-2</sup>

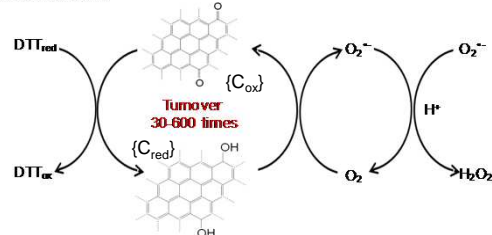
- Both HVO and diesel soot are **strongly reducing** and have **weakly basic** (vinylogous pyrone) structures at the interface in contrast to a high surface area synthetic amorphous carbon (Printex XE-2B) and soot reference materials annealed at high temperature (GTS-6 and 80).

### Catalytic ROS production in presence of DTT, NP and dissolved O<sub>2</sub>

- Based on Fig. 3, we propose a rate law with a quadratic dependence of the initial reaction rate on [O<sub>2</sub>].

$$-d[O_2]/dt = k[O_2]^2 [DTT] [NP]$$

- This rate law corresponds to a heterogeneous catalytic chain reaction with the following mechanism:



- The **rate-limiting step** corresponds to the oxidation of {C<sub>red</sub>} (tentatively identified as a vinylogous hydroquinone) rather than the reduction of an oxidized surface site {C<sub>ox</sub>} (tentatively identified as a quinone).
- The turnover of 30-600 times corresponds to the ratio between the total amount of O<sub>2</sub> consumed and the number of strongly reducing sites (NO<sub>2</sub> probe gas) on the particle surface, variability shows irreversible catalyst loss.

## Conclusion / Perspectives

- The mechanism of antioxidant consumption by carbonaceous NP's is a **heterogeneous catalytic chain reaction** using dissolved O<sub>2</sub> as oxidant. Redox cycling occurs between corresponding pairs of oxidized/reduced hydrocarbons whose structures are spatially extended.
- Two soots from internal combustion engines (HVO and Diesel soot) have a massive amount of reducing and weakly basic surface functional groups. **We expect a high catalytic activity for these two soots** compared to the other synthetic amorphous and annealed carbon studied.
- The presence of quinone/hydroquinone structures affords the possibility of the occurrence of **environmentally stable free radicals**, possibly long-lived peroxides.