

Surface Composition of Diesel Soot using Heterogeneous (gas-surface) kinetics of reactive Probe Gases

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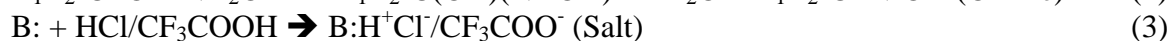
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Introduction

The reactivity of a nanoparticle (NP) including the interaction with biological membranes or substrates leading to deleterious health effects significantly depends on the molecular surface composition as it is the “gateway” to understanding and controlling chemical reactivity of NP’s. There are many ways to characterize the surface of NP’s. Examples include the investigation of the thermal behavior such as pyrolysis and thermogravimetric measurements, the extraction behavior of NP’s in terms of the adsorbed (extractable) organic phase vs. the elemental carbon content (OC/EC), WSOC, WinSOC and other extraction strategies, elemental analysis (C,H,N,O), surface spectroscopies (XRD, EELS, XPS, EX-AFS, others) and Imaging techniques (ESEM, HRTEM). The present contribution proposes to apply a chemical way to characterize the surface of NP’s by making use of the chemical reactivity of surface functional groups of NP’s gauged by suitable probe gases which “see” only one monolayer or so.

Results and Discussion

A Knudsen flow reactor was used for the investigation of the heterogeneous reaction of the probe gases with the NP substrate presented either on a loaded Teflon membrane filter or as loosely packed powder housed in a FEP Teflon-coated sample cup. The use of a Knudsen flow reactor is suitable because it favors gas-wall collisions compared to gas-gas collisions owing to the low total pressure in the range 10^{-5} to 10^{-2} mbar leading to large mean free paths. Changes in the molecular beam intensity monitored by phase-sensitive molecular beam modulated electron impact mass spectrometry (MBMMS) are recorded upon exposure of the probe gas to the NP sample material. The number of probe molecules “lost” to the sample is expressed as a fractional number of formal monolayers of the probe gas on the NP surface under conditions of known BET surface of the NP sample. The following reactions are thought to occur upon interaction with the used probe gases:



Equation (1) forms a salt following gas-surface heterogeneous neutralization of trimethylamine. In case of an organic aerosol or soot substrate the acidic site is identified with a carboxylic surface group that represents totally oxidized carbon. In Eq. (2) hydroxylamine probes partially oxidized surface sites such as aldehydes or ketones leading to the corresponding oximes for organic substrates. Equation (3) describes the probing of basic surface sites, either Brönsted or Lewis bases B: Equation (4) describes the redox reaction of a strong (O_3) and a weak (NO_2) oxidizer interacting with a weakly reducing and a strongly reducing surface site, $-C_{red}$, respectively.

Diesel soot from incomplete combustion of Diesel and Biodiesel (Hydrotreated Vegetable Oil, HVO) has been collected from an exhaust manifold of a modern common rail Diesel engine [1]. The focus will be placed on the results of three substrates, namely Diesel, HVO and a commercial amorphous carbon (PRINTEX XE2-B) as a benchmark, using both NO_2 and O_3 as probe gases that probe the reducing power of surface functional groups of varying redox potential (strongly reducing and the sum of all reducing surface functional groups). By the same token, the initial uptake coefficient γ_0 of the probe gas kinetics may be retrieved. HVO and Diesel soot samples reacted with all probe gases indicating the presence of different functionalities on the same aerosol surface. In comparison to the reactivity of amorphous carbon PRINTEX XE2-B the investigated soot samples had a significantly higher surface density of reducing functional groups reacting with the O_3 probe gas by a factor of 10 to 30. Noteworthy is the fact that these reducing groups were practically all strongly-reducing because the O_3 and NO_2 probe gas experiments resulted in identical surface densities. These strongly-

Table displaying experimental results of Surface Titration using six reactive probe gases. The units of N_M are molecule mg^{-1} and molecule cm^{-2} , respectively. FM corresponds to a formal monolayer in terms of a fraction of FM. Multiplication by 100 yields percent monolayer coverage.

	Surface BET / m^2 g^{-1}		$N(CH_3)_3$	NH_2OH	CF_3COOH	HCl	O_3	NO_2
PRINTEX XE2-B	1000 ^a	$N_M mg^{-1}$	$3.16 \cdot 10^{16}$	$8.51 \cdot 10^{16}$	$5.66 \cdot 10^{16}$	$2.27 \cdot 10^{16}$	$8.79 \cdot 10^{16c}$	$5.18 \cdot 10^{16c}$
		$N_M cm^{-2}$	$3.16 \cdot 10^{12}$	$8.51 \cdot 10^{12}$	$5.66 \cdot 10^{12}$	$2.27 \cdot 10^{12}$	$8.79 \cdot 10^{12c}$	$5.18 \cdot 10^{12c}$
		% FM	0.88	1.08	1.42	0.26	1.19 ^c	0.73 ^c
DIESEL SOOT	333.18 ^b	$N_M mg^{-1}$	$5.20 \cdot 10^{16}$	$3.44 \cdot 10^{16}$	$9.31 \cdot 10^{16}$	$1.76 \cdot 10^{16}$	$8.25 \cdot 10^{17c}$	$5.49 \cdot 10^{17c}$
		$N_M cm^{-2}$	$1.56 \cdot 10^{13}$	$1.03 \cdot 10^{13}$	$2.79 \cdot 10^{13}$	$5.29 \cdot 10^{12}$	$2.48 \cdot 10^{14c}$	$1.65 \cdot 10^{14c}$
		% FM	4.33	1.31	6.98	0.62	33.45 ^c	23.21 ^c
HVO SOOT	438.57 ^b	$N_M mg^{-1}$	$1.59 \cdot 10^{17}$	$1.10 \cdot 10^{17}$	$1.71 \cdot 10^{17}$	$2.93 \cdot 10^{16}$	$3.63 \cdot 10^{17}$	$3.40 \cdot 10^{17}$
		$N_M cm^{-2}$	$3.63 \cdot 10^{13}$	$2.52 \cdot 10^{13}$	$3.90 \cdot 10^{13}$	$6.68 \cdot 10^{12}$	$8.27 \cdot 10^{13}$	$7.76 \cdot 10^{13}$
		% FM	10.09	3.19	9.74	0.78	11.18	10.93

reducing reactions may elicit distinct catalytic redox reactions in biological systems and may lead to unexpected health effects which are in the process of being explored in more detail. The above-displayed Table presents the detailed uptake experiments to be discussed.

[1] A. Tapia et al., submitted to *Environ. Sci. & Technol.* (2015).