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Internally mixed multicomponent soot: Impact of different salts on soot structure and thermo-chemical properties



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ABSTRACT

An often referred feature of ambient and combustion aerosol samples is their ratio of elemental carbon (EC) to organic carbon (OC). Thermo-optical methods are commonly used to determine this ratio. As those methods generally consist of a heating step under inert atmosphere for OC quantification and a consecutive combustion step under oxidative atmosphere for EC quantification, combustion catalysts may drastically impact the measured EC/OC value. Such catalysts may be minerals, e.g. inorganic salts or oxides, that are mixed with the soot and may stem from various sources.

In this study, the impact of varying content of different salts internally mixed with soot on soot structure and oxidation reactivity was studied. For this purpose, a novel method for preparation of model soot aerosols internally mixed with different inorganic salts (CaSO_4 , $\text{Ce}(\text{SO}_4)_2/\text{CeO}_2$, Na_2SO_4 , or NaCl) at different contents was applied by spraying aqueous salt solutions into a propane diffusion flame. Proof of production of internal mixtures of soot with the different salts was given by scanning electron microscopy (SEM). Raman microspectroscopy (RM) was utilized to characterize the soot structure. Soot oxidation reactivity was analyzed by temperature-programmed oxidation (TPO). It could be proven that doping of the soot with inorganic salts does not impact the soot structure. However, soot oxidation reactivity is strongly enhanced with increasing salt content resulting in a TPO emission maximum shifted by up to 200 K towards lower temperatures. Our results pose questions on the feasibility of thermo-optical methods for the determination of EC/OC values of carbonaceous aerosols in the presence of internally mixed minerals.

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1. Introduction

Ambient aerosols and specifically combustion-derived aerosols are often characterized by their content of elemental carbon (EC) and organic carbon (OC), which are determined by thermo-optical methods (Ram & Sarin, 2011; Watson et al., 2005). Besides organic and elemental carbonaceous materials, ambient aerosols may also contain inorganic materials. The inorganic materials may be among others oxides, sulfates, nitrates, or chlorides of alkali and earth alkali elements (mostly Na, Mg, Ca), metals (mostly Al, V, Fe, Ni, Cu, and Zn), and Si. They may stem from various sources such as primary emissions like wood or oil combustion, industry, sea spray, or mineral (soil) dust as well as secondary aerosols (Artaxo et al., 1999; Viana et al., 2008).

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In the specific case of traffic-generated soot aerosols, fuel-borne metal-based catalysts may be a source of metal oxides such as iron or cerium oxide (Naschke et al., 2008; Song et al., 2006; Vouitsis et al., 2008). Also the lubricant in marine or automotive engines may contain additives in order to improve its performance. Such additives may be surfactants such as calcium sulfonate (Hudson et al., 2006), which decompose to form calcium sulfate CaSO_4 during engine combustion (McGeehan et al., 2009). Not only additives but also impurities in fuel and lubricant are a source of minerals mixed in engine exhaust aerosols. Particularly, oxides and sulfates of iron, vanadium, nickel, zinc, and calcium can be found at significant concentrations in the exhaust of ship engines using low grade heavy fuel oil (Lyyr nen et al., 1999; Moldanov  et al., 2013). Such additives and impurities in the fuel and/or lubricant are directly introduced into the soot formation process. Thus, the generated soot particles consist partly of soot and minerals and the soot possesses a very intimate contact to the minerals. We therefore term this type of soot as soot internally mixed with minerals. This definition is analogous to Adachi & Buseck (2008) who examined internally mixed soot, sulfates, and organic matter in ambient aerosol particles. Adachi & Buseck (2008) define soot particles coated with organic matter or sulfate as well as internally mixed soot.

There exist several studies on the effect of various catalysts on the oxidation of carbonaceous material, specifically soot (Stanmore et al., 2001). Some of these studies used doped fuels or flames for the production of internally mixed soot aerosols. In such studies mainly Ce-, Fe-, Pb-, Cu-, V-, Mn-, and/or K-based catalysts were used to form (mixed) oxides of these elements internally mixed with soot (Bladt et al., 2012; Bonnefoy et al., 1994; Kim et al., 2010; Laheye et al., 1996). However, to our knowledge there are no publications on the systematic laboratory production and characterization of soot internally mixed with non-oxide minerals such as CaSO_4 , Na_2SO_4 , or NaCl.

In contrast, most studies cover physically mixed soot with potential catalysts yielding in externally mixed multi-component soot. To produce this externally mixed soot, the mineral species were mixed with the mineral-free soot after the actual soot formation process generating a loose contact between the soot and the catalyst that is not as intimate as for internally mixed soot. Thus, externally mixed soot consists of separate soot particles and mineral particles, whereas internally mixed soot contains particles, which are composed of both soot and minerals. In the mentioned studies of externally mixed soot, soot was either impregnated with aqueous catalyst solutions (Castoldi et al., 2009; Matarrese et al., 2008) or mechanically mixed with the catalyst (Ciambelli et al., 1996; Neeft et al., 1998). Neeft and co-workers additionally differentiated between “loose” and “tight” contact for externally mixed soot. The former was produced by loose mixing of soot with the catalyst, for the latter both components were milled. Several metal catalysts (MoO_3 , Fe_2O_3 , V_2O_5 , etc.) were tested and ranked by Neeft et al. (1996). In general, tight contact yielded in higher oxidation reactivity than loose contact.

Furthermore, for both soot externally mixed with metal oxides at tight contact (Ciambelli et al., 1996; Neeft et al., 1998) as well as internally mixed iron oxide-containing soot (Bladt et al., 2012; Kim et al., 2010), a significant fall in combustion temperatures with increasing catalyst content was observed. Reaction rates decreased significantly with increasing mass ratio of catalyst to soot (Ciambelli et al., 1996; Kim et al., 2010).

For graphite oxidation, alkali salts are also known as catalysts besides metal oxides (Patai et al., 1952). However, we are not aware of any study systematically demonstrating the catalytic effect of diverse salts like CaSO_4 , Na_2SO_4 , or NaCl internally mixed with soot on its oxidation as we have done with this study.

Despite the knowledge of the catalytic effect of certain minerals on soot oxidation, the feasibility of thermo-optical methods for the quantification of EC and OC in aerosol samples is rarely questioned. Depending on the applied protocol of such methods, e.g. IMPROVE (Chow et al., 1993), NIOSH 5040 (National Institute of Occupational Safety and Health, 1999), etc., the aerosol filter samples are firstly heated under inert atmosphere (usually He) up to a certain temperature to quantify OC. Secondly, the samples are reheated under oxidative atmosphere (1–100% O_2 in He depending on protocol) for EC quantification. In some protocols, the effect of OC charring to form EC during the first heating step under inert atmosphere is accounted for by a so-called pyrolysis correction. Thereby, the thermo-optical reflectance (TOR) and/or the thermo-optical transmittance (TOT) of laser light illuminating the filter sample are monitored. This pyrolysis correction shifts the split point between OC and EC evolution to the point where the reflectance or transmittance reaches its initial level (Watson et al., 2005). Thermo-optical analyses of ambient aerosols have been numerous published and according to Watson et al. (2005), it is doubtful that future carbon comparisons would lead to more information unless they include components that systematically study the effects of sample properties and the analysis variables.

For this reason, we present a detailed and systematic characterization of internally mixed soot containing different salts concerning soot structure and thermo-chemical properties. Thereby, useful conclusions on the applicability of thermo-optical methods for mineral-containing soot can be drawn. Particularly, it is possible that the EC/OC ratio can be severely reduced in presence of salts due to a reduction in oxidation temperature of EC and an enhancement in OC charring as found by Wang et al. (2010) using the NIOSH 5040 protocol for externally mixed multicomponent soot. For this purpose Wang et al. (2010) deposited metal particles on top of filters loaded with diesel exhaust particles producing external mixtures of both components. According to Wang et al. (2010) the split point correction is more dependent on changes in EC oxidation temperature than it is on OC charring. In further studies Wang et al. (2012) quantified black carbon in ice and snow following the IMPROVE TOR protocol. It could be demonstrated that inorganic material can change its optical properties during thermal treatment and thus can interfere with pyrolysis correction.

The aim of this study is to systematically demonstrate the catalytic effect of diverse salts on soot oxidation. For this purpose, we developed a new method of producing internally mixed model soot aerosols by spraying aqueous solutions of

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