Aerosol Science 40 (2009) 55 – 64

Contents lists available at ScienceDirect

Aerosol Science

journal homepage: www.elsevier.com/locate/jaerosci

TEM study on volatility and potential presence of solid cores in nucleation mode particles from diesel powered passenger cars

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ARTICLE INFO

Article history:
Received 7 April 2008
Received in revised form
8 August 2008
Accepted 20 August 2008

Keywords:
Nucleation particles
Diesel particles
Particle morphology
Particle volatility
TEM
Size distribution

ABSTRACT

Nucleation mode particles were investigated for their morphology using TEM and the presence or absence of solid cores was addressed. At cold start idle nucleation particles were observed in the exhaust of a diesel passenger car. These particles occurred with both low and high S fuel and were only partly volatile in a thermodenuder, which indicates that the composition was not sulfate and as derived from TEM/EDX (transmission electron microscopy/energy dispersive X-ray analysis) probably not ash. It could be high boiling hydrocarbons, or primary soot particles. With all fuels at warm idle no nucleation particles and only soot particles were observed in the SMPS and the TEM. With 3.0×10^{11} s^{-1} the total soot particle number during idle was much less than during driving, e.g. at 120 km h^{-1} the emission rate was 6.7×10^{12} s^{-1}. At high load and high S fuel 10–20 nm nucleation particles were observed by SMPS and TEM. A thermodenuder at 280 °C and TEM showed that all nucleation particles were volatile. EDX gave a weak S-signal only. Some nucleation particles contained smaller spots (1–3 nm) with a very high contrast, which might be due to heavy elements. However, under the electron beam of the TEM these spots disappeared and EDX analysis was not possible. With low S fuel at 120 km h^{-1} only soot particles and no nucleation particles were observed.

1. Introduction

The smallest particles found in the atmosphere are the so-called nucleation mode particles. Although the mass concentration of these particles is insignificant due to their small size, nucleation mode particles can dominate the number of particles under certain conditions. No strict definition of the size of nucleation mode particles exists, but they are typically 10–30 nm (Baron & Willeke, 2001; Kittelson, 1998) and can be formed due to photochemical reactions in the atmosphere or by condensation of combustion products. Due to their transient nature nucleation mode particles are significant only in the vicinity of sources, for example freeways. Recently, solid ultrafine particles which are smaller than 100 nm of size have raised considerable interest because of their potential adverse health effects (Donaldson, Li, & MacNee, 1998; Harrison, Jones, & Collins, 1999; Shi & Harrison, 1999; Wallace, 2000; US-EPA "Air Quality Criteria for Particulate Matter", 2004). If liquid nucleation particles contained solid cores, they would also have the potential for health concerns. Despite this, the physico-chemical nature of nucleation mode particles from combustion is only poorly understood.

It has been shown that formation of nucleation particles in diesel passenger car exhaust is related to high fuel sulfur content, high engine load and the presence of an oxidation catalyst (Maricq, Chase, Xu, & Laing, 2002; Vogt, Scheer, Casati, & Benter, 2003). Schneider et al. (2005) found that nucleation mode particles from diesel combustion are composed of sulfate and organic

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doi:10.1016/j.jaerosci.2008.08.002

material, whereas the organic species only condense on pre-existing sulfuric acid/water clusters. However, there has also been some speculation on solid residuals, like soot, metal oxides or low volatility organic compounds (Sakurai et al., 2003). Very recently, the formation of nucleation mode particles was also confirmed at idle conditions (Kubo, Kondoh, Suzuki, Mitsuoka, & Ito, 2005; Vogt, Kirchner, Scheer, & Kaegi, 2005).

Volatile nucleation particles were also observed in the exhaust of a particle trap equipped diesel and a direct injection gasoline vehicle (Mohr, Forss, & Lehmann, 2006). The nucleation mode appeared only at high load and not at 50 km h^{-1} with road load. The nucleation particles evaporated in the TEM with different rates pointing at a composite nature of the particles with hydrophilic and hydrophobic components (Mathis, Kaegi, Mohr, & Zenobi, 2004). Nucleation particles at idle and during deceleration were observed by Kubo et al. (2005) using a direct injection four cylinder engine. The composition was determined to be oxygenated hydrocarbons and the formation process was proposed to be homogeneous nucleation. Using AFM a hard center was not observed close after sampling but appeared during the process of evaporation of the particle in the vacuum of the instrument. It was concluded that under idling and deceleration conditions the nucleation particles were liquid like and did not contain a solid core. Solid particle cores were detected only when oil was added to the fuel and lubricating oil additives with inorganic compounds were used. The importance of dilution conditions and the choice of diluter were documented by Lyyräanen, Jokiniemi, Kauppinen, Backman, and Vesala (2004). A clear nucleation mode was obtained with a setup which provided fast cooling and mixing similar to atmospheric dilution. A comparable dilution setup was used in this study, which aims at simulation of atmospherically relevant conditions and particle formation.

In this study we focus on the nucleation mode particles, occurring under different operating conditions. The number, size and volatility of the particles were determined using two SMPS systems and an optional thermodenuder (TD), described by Wehner, Philippin, and Wiedensohler (2002). Nucleation particles were produced during idle and during steady state driving. The size distributions had different volatility and were changing with time. Detailed analysis of single particles was performed with a transmission electron microscope (TEM). For that purpose, particles were collected directly on TEM grids and investigated for their morphology. For nucleation particles produced during idle and during steady state driving the presence or absence of solid cores was addressed.

In the anticipated European regulation particle number measurements will be required from 2011 onwards. By definition volatile particles will be removed and particles smaller than the cut-off diameter of 23 nm will not be counted. From this point of view it is important to investigate if small solid cores were present at relevant numbers.

2. Experimental

2.1. Setup

All testing was done at the Ford Research Center in Aachen, Germany using a chassis dynamometer with a 48 in (1.22 m) diameter role ("Compact Rolle", AVL, Kiel, Germany), max. 186 kW break power, max. speed 200 km h^{-1}, and loss compensation. For the experiments a model year 2002, 1.8 L, 74 kW (100 hp) diesel passenger car was used, which was equipped with a turbo charger, direct injection, exhaust gas recirculation and an oxidation catalyst. The vehicle was Euro 3 certified with particulate matter mass emission of ~14–20 mg km^{-1} and the inertia weight for road simulation was 1360 kg. The fuel was a European Reference Fuel with sulfur < 10 ppm and aromatics content of 23.5%. For high sulfur experiments the fuel was doped with a sulfur containing mixable organic compound to 310 ppm.

2.2. Dilution and particle sampling

The exhaust gas was diluted in two steps to simulate atmospheric dilution (Fig. 1). The first step was a self-constructed in situ diluter which was mounted directly into the tailpipe (Casati, Scheer, Vogt, & Benter, 2007). The diluter was optimized to simulate atmospheric dilution and was held at constant 20 °C using a thermostat which pumps water through a thermostatic jacket of the diluter. By setting the dilution air flow and the diluted exhaust flow with flow controllers the amount of sampled exhaust gas and the dilution factor could be calculated. The second step was a commercial Rotating Disk Diluter (RDD) type MD19–2E (Matter Engineering AG, Wohlen, Switzerland). The secondary dilution factors were set between 37.5 and 83.3 by varying the rotation speed and changing the disk if necessary.

Casati et al. (2007) showed that the laboratory results compared well to "real world" dilution measured in the exhaust plume, if the primary dilution factor was approximately 10 and the temperature was set to constantly 20 °C.

To collect the ultrafine particles two different setups were used. In the so-called 'conventional' setup described in Mavrocordatos, Kaegi, and Schmatloch (2002) and Mathis et al. (2004), a TEM grid (lacy carbon) was attached onto a Nucleopore (NP) filter (0.4 μm pore diameter). The diluted exhaust gas was drawn through the NP filter and the ultrafine particles were deposited by diffusion on the TEM grid. Alternatively, ultrafine particles were collected using a specifically designed electrostatic sampler (Fierz, Kaegi, & Burtscher, 2007). Particles were electrically charged using a corona charger and then deposited in an electric field directly on TEM grids. The schematic layout of the experimental setup is given in Fig. 1.

Two types of SMPS (TSI Inc.) were used to record the particle size distributions. A combination of a long DMA 3071 and a counter CPC 3010 covering the particle size range between 10 and ~300 nm was used to record the size distributions of the