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Various carbon dust particles

Studies on thermal behaviour

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Abstract Nano-sized carbon dusts are suspected of having negative effects on human health. An exact characterization of such particles is necessary to understand possible toxic effects, i.e. in the lung. Observed by transmission electron microscopy (TEM), the carbon dusts are a composite of very small primary particles and larger agglomerates of these. A differentiation of the primary particles and agglomerates according to source is not possible by TEM, however, thermogravimetry investigations in synthetic air atmosphere are helpful. Standardized carbon black and graphite show a single-step oxidation behaviour, whereas ethene soot and diesel soot, for example, show more complex-reaction mechanisms. The results of ethene soot exemplarily demonstrate the oxidation mechanism. In addition to the oxidation reaction to carbon dioxide, a sintering process takes place. To confirm the oxidation mechanism, thermal behaviour of ethene soot has been simulated by kinetic modulation using a three-step reaction mechanism of *n*-th order. The reaction order indicates a complex mechanism for the first-reaction step. For the second and third-reaction step, a phase boundary mechanism could be suggested.

Keywords Carbon dusts · Ethene soot · TEM · Thermal analysis · Kinetic analysis

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Introduction

Nanotechnology is considered to be the key technology of the twenty-first century. It is expected that applications will not only be found in many areas of industry, but also in connection with new therapeutic and diagnostic procedures in the medical field. Nanoscale structures with dimensions entirely or partially smaller than 100 nm can actually generate new functionalities and properties. Nanoparticles can either be produced by means of "bottom up" technique from gas and liquid phase reactions, or by means of the "top down" technique by grinding or deforming of larger particles. Nanoparticles are also increasingly formed in modern combustion processes such as in diesel engines.

Beside the studies regarding the reaction mechanism, it is urgently necessary to clarify the health risks involved with nanoparticles and nanotubes [1]. Nanoparticles can easily be inhaled into the lungs and can reach even the alveoli, due to their small size. Once deposited there, the particles can no longer be removed by the biomechanism responsible for cleaning the upper and middle respiratory tracts ("muco-ciliary clearance") (Fig. 1). Particles deposited in the alveoli can be considered as "biostable" dust particles. In order to dissolve those particles, complex biochemical processes may take place, which increase the potential for inflammation and even the risk of lung cancer. Penetration into the interstitium may occur additionally, hence allowing the nanoparticles to become systematically distributed.

To discuss the dangers of airborne biostable dust particles to human health in more detail, state-of-the-art characterization methods are required. Here, electron microscopy and thermal analysis combined with gas analysis may be taken into account [2, 3]. A comparison of diesel soot and carbon black showing similarities was done previously [4].

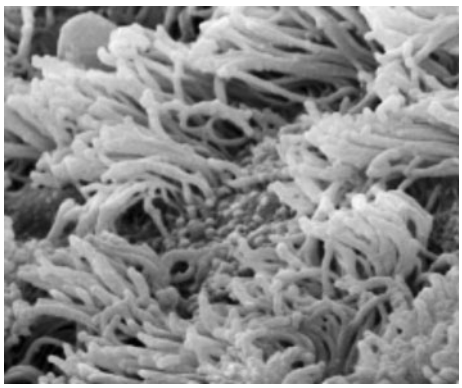

Fig. 1 Mucociliary clearance by cilia in the bronchiole wall (SEM; magnification ×5,000)

In this study, carbon dusts of carbon black, ethene soot, diesel soot and graphite were used for a more detailed study of their morphology and oxidation behaviour.

Experimental

Commercially available carbon black (Printex 90, Degussa, Germany) and graphite FE 504 (Schunk Group, Germany) were used. Further ethene soot was produced in laboratory scale by burning a mixture of ethene gas and synthetic air in a modified forced-air burner. Diesel soot has been collected from the exhaust line of a diesel engine (type euro 2).

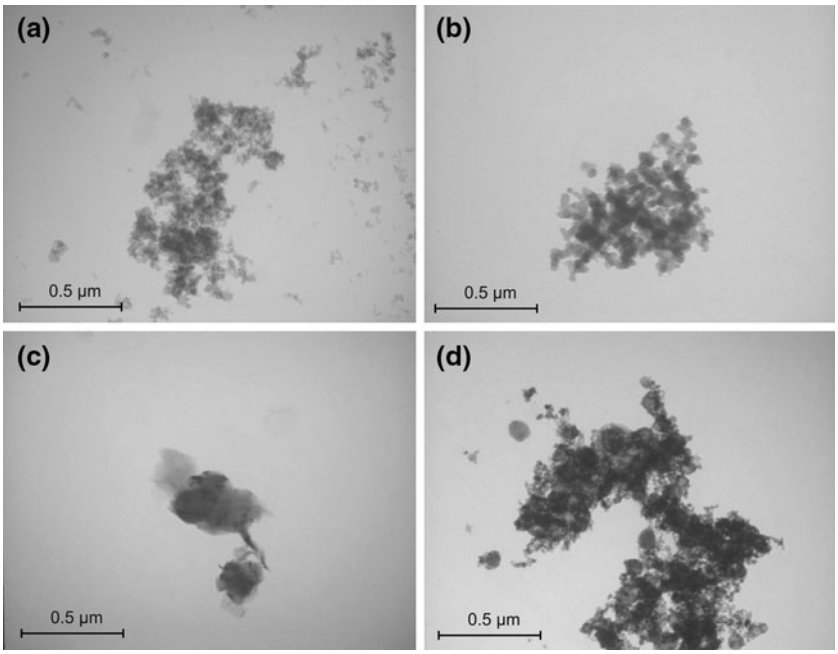

Fig. 2 TEM images of carbon black (**a**), ethene soot (**b**), graphite (**c**) and diesel soot (**d**) (magnification ×40,000)

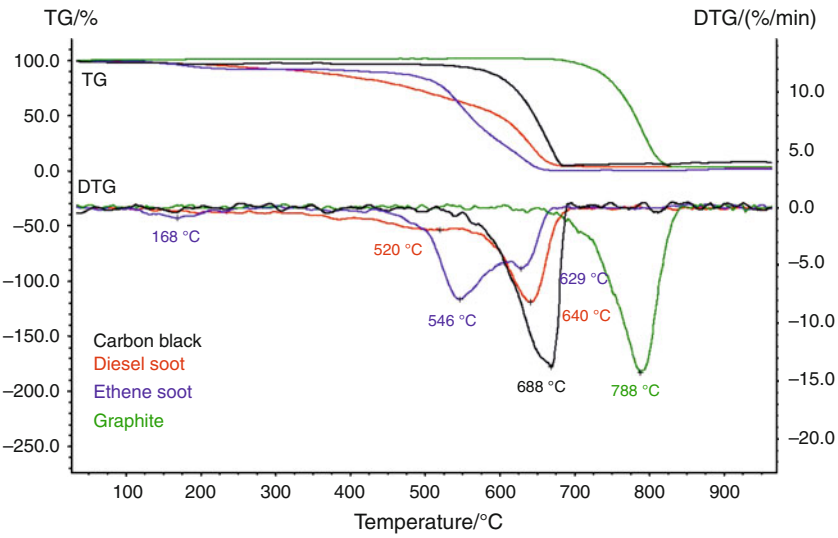

Fig. 3 TG and DTG results of carbon black, diesel soot, ethene soot and graphite (heating rate 10 K/min)

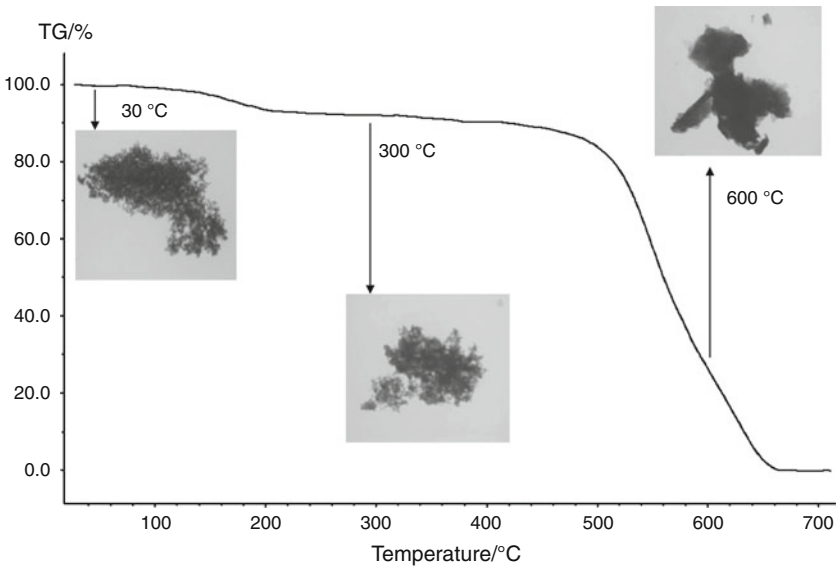

Fig. 4 Ethene soot oxidation, TG and TEM results (magnification ×40,000)

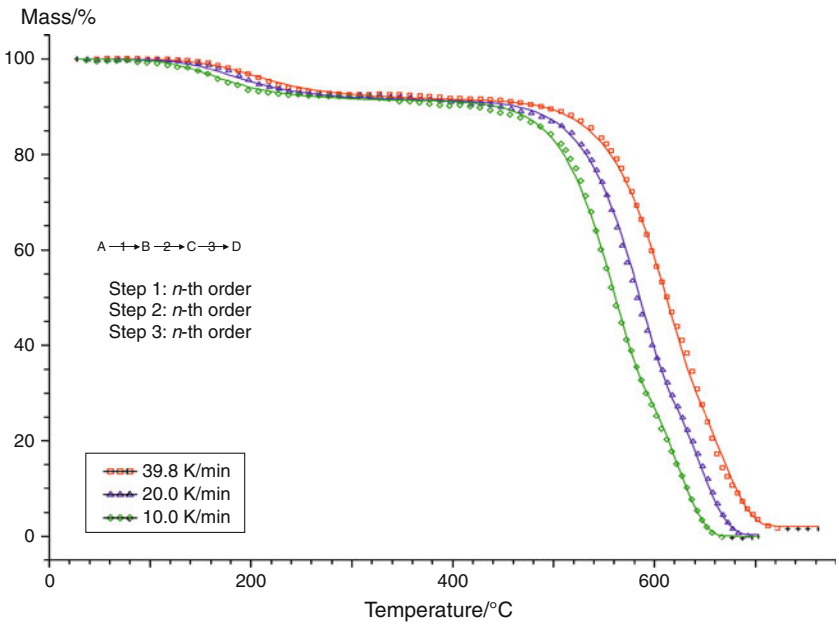

Fig. 5 Comparison of measured data (*symbols*) and calculation data by non-linear regression (*lines*) of ethene soot

Transmission electron microscopy (TEM) analysis was done using a transmission electron microscope H-600 (Hitachi, Japan).

Thermogravimetry (TG) measurements were carried out with different heating rates using corundum crucibles under air atmosphere employing a thermobalance TG 209 F1 Iris (NETZSCH-Gerätebau, Germany).

For kinetic analysis, the software "Thermokinetics" (NETZSCH-Gerätebau, Germany) was used.

Results and discussion

Transmission electron microscopy

The results of the TEM investigations are demonstrated in Fig. 2. All dusts resulted in agglomerates (diameter, ~1 µm) composed of primary particles (20–50 nm). In the case of graphite, aggregates (diameter, ~0.5 µm) were observed. The various dusts seem optically identical,

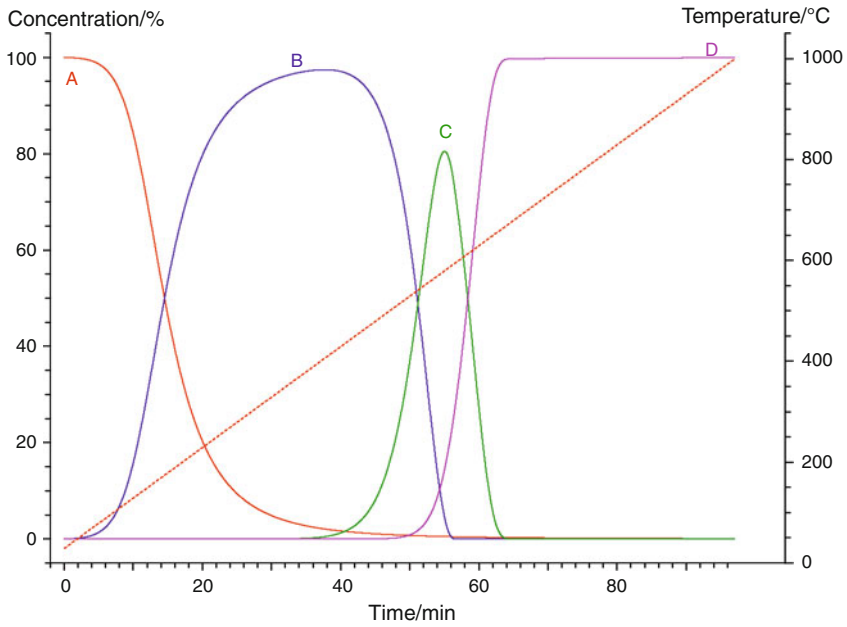

Fig. 6 Calculated concentrations of the formal reactants of ethene soot oxidation

therefore, electron microscopy does not allow a more detailed differentiation.

Thermogravimetry

TG measurements were done under synthetic air atmosphere with a heating rate of 10 K/min (Fig. 3). In contrast to the TEM results, significant differences for all four carbon dusts are detected. Carbon black oxidizes in a single-step reaction, completed at 700 °C. The oxidation behaviour of graphite is comparable to carbon black. However, the DTG minimum is shifted to higher temperatures which may be due to the aggregated product.

The oxidation behaviour of ethene soot and diesel soot detected by means of thermogravimetry differs significantly compared to carbon black and graphite. A three-step TG signal is observed for ethene soot oxidation (three DTG minima). A two-step oxidation behaviour is observed for the diesel soot. Between 200 and 600 °C, an increasing reaction rate indicates a complex oxidation process.

The variation of the particle morphology during the oxidation process of ethene soot is shown by TEM measurements (Fig. 4). The samples have been taken after stopping the TG experiment at different temperatures (30, 300 and 600 °C). At 30 °C, small primary particles are clearly visible. At 300 °C, the number of primary particles is decreased due to agglomeration. At 600 °C, nearly no primary particles exist any more. Here, aggregates are formed as a result of a sintering process.

Table 1 Kinetic data of the non-linear regression of ethene soot

Steps	Type	Parameter	Value
1	*n*-th order	log A1/s^{-1}	4.5
		E1/kJ mol^{-1}	56.6
		React. ord. 1	2.8
2	*n*-th order	log A2/s^{-1}	7.4
		E2/kJ mol^{-1}	154.4
		React. ord. 2	0.8
3	*n*-th order	log A3/s^{-1}	10.0
		E3/kJ mol^{-1}	209.9
		React. ord. 3	0.8

Kinetic analysis of ethene soot

TG measurements of ethene soot were done under synthetic air atmosphere with different heating rates. These experiments can be evaluated by using a special kinetic software (Netzsch Thermokinetics, Germany). The evaluation of the kinetic parameters can be done by applying the model-free methods (ASTM 698, Friedman, Ozawa, Flynn, Wall) and model-based methods [5]. Here, the parameters fit the experimental data by multivariate non-linear regression. The three-step consecutive model of *n*-th order mechanism (closed lines) describes the experimental TG result excellently (symbols, Fig. 5) as opposed to former kinetic results of carbon dusts using a first-order approach [6–8].

Activation energy, pre-exponential factor and reaction order were obtained by means of kinetic evaluation (Table 1).

The first-reaction step shows a reaction order of 2.8 that indicates a complex oxidation process. This reaction step is due to a starting oxidation. The mechanism of the oxidation of solids in general is diversified. First, the reaction occurs at the surface of the particles, whereas the second (reaction order, 0.8) and third steps (reaction order, 0.8) are related to phase boundary reactions that are due to oxidation and aggregation [9, 10].

A prediction of the reactants of the ethene soot oxidation, calculated with applying the above discussed three-step consecutive model, does underline the statement of the aggregation and agglomeration processes (Fig. 6). "A" represents the initial particles. Then, due to agglomeration, reactant "B" is formed. "C" implements the aggregated particles. "D" can be seen as the CO_2.

Conclusions

Carbon black, graphite, ethene soot and diesel exhaust particles consist of agglomerates of toxicologically relevant ultrafine particles that can be barely differentiated from one another. In contrast to electron microscopy, thermogravimetry can be used to differentiate quickly and reliably between the carbon dusts. Even the use of small sample amounts (<1 mg) lead to reliable thermogravimetric results. Carbon black and graphite show a clear one-step oxidation behaviour. The oxidation behaviour of ethene soot is comparable to the behaviour of soot obtained from diesel engines. Both are characterized by a more complex mechanism. The use of electron microscopy can help to visualise the change of the morphology of the particles and to understand the oxidation processes. The aggregation due to sintering processes is visible. Kinetic analysis emphasizes this thesis. The reaction order is basically derived by phase boundary reactions for the later oxidation steps, whereas, the mechanism of the first step is caused by more complex processes.

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