Chapter 1

Introduction

This thesis concentrates on nano’s, not a new topic but a new approach how to tailor the size distributions and properties. Needless to say that nanoparticles and nanoclusters attract considerable interest in scientific research and industrial applications including microelectronics, optics, catalysis, medicine, biology due to their unique size-dependent physical and chemical properties [1-5]. Nevertheless, an important issue is whether we are able to control the size distribution to tailor certain physical and chemical properties and whether we are able to study the structural aspects in detail. Physical and chemical properties may be determined not by the mean size but by the largest size and controlling and studying the width of the size distribution in relation to properties is of utmost importance. The usage of the term nano in this thesis needs also a further explanation.

The term nanoparticle was commonly used already in the early 1990s together with the related concepts, nanoscaled or nanosized particle. Before that period rather general terms, such as submicron and ultrafine particles were used. Now the term nanoparticle generally points to particles with diameters about or smaller than 100 nm. A closely related but not identical concept, cluster, frequently indicates smaller nanoparticles with diameters less than 100 nanometers having distinguishable properties. It is like a separate state in between atomic and bulk. In the following the terms cluster, particle and nanoparticle we will is used interchangeably.

The driving force behind these developments is to explore novel materials with entirely new properties by tailoring the structure of materials at the nanoscale. Nanotechnology has also an ecological ambition to reduce the amount of undesirable waste [5]. To tune size-dependent properties of nanoparticles the formation process needs to be controlled [6]. However, producing such materials, presents its own challenges related to understanding the rules that govern their assembly and their properties [7].
Nanoparticles are created by two major techniques: *top-down techniques*, which are shrinking the size of the particles to the nanometer scale (e.g. ball milling, also known as mechanical attrition); but also so-called *bottom-up techniques*, in which individual atoms from solution or gas phase form clusters. All the techniques used can be divided into chemical and physical ones [2].

In this thesis we consider nanoparticle formation in the gas phase by (i) gas aggregation technique and (ii) synthesis in flames. In the gas aggregation technique a supersaturated atomic vapor is created by the vaporization of the precursor material in an aggregation chamber filled with a buffer inert gas [8]. Plasma sputtering with a magnetron ion source provides a method of vaporizing a wide range of materials [9]. Clusters grow in the aggregation chamber until the mixture of gas and clusters is released through an aperture into a surrounding vacuum chamber. Nanoparticles can be produced naturally in almost every flame. Today this phenomenon is used for gas phase combustion synthesis of a variety of inorganic oxides in the form of fine particles amounting to millions of tons annually [10]. They are used industrially as pigments, opacities, catalysts etc. Experimental, modeling and industrial aspects of particle formation in flames can be found in a number of review papers [11-16].

In Chapter 2 methods for producing nanoparticles are reviewed. To produce one component metallic nanoclusters the setup was built using a NC200-UHV nanocluster source manufactured by Oxford Applied Research. In this chapter we also describe equipment used to study the formation of SiO$_2$ nanoparticles during combustion of a premixed stoichiometric methane/air mixture doped with hexamethyldisiloxane (C$_6$H$_{18}$Si$_2$O, denoted as L2).

Chapter 3 summarizes the various experimental methods that have been employed during this thesis work so as to characterize nanoparticles. The principal technique used is high resolution transmission electron microscopy (HRTEM). Besides HRTEM this chapter presents a concise introduction to scanning electron microscopy (SEM) and to the important issues of image processing and analysis of nanostructured materials.

Nucleation and growth of nanoparticles are affected by several parameters, such as the temperature, the residence time of particles in the aggregation chamber and the ratio of the material gas to the inert gas. By changing the experimental conditions the particle morphology and the particle size distribution (PSD) can be controlled to produce nanoparticles with required properties. Frequently the effect of experimental conditions on nanoclusters formation is difficult to predict and certain properties of nanoclusters cannot be measured directly. For that reason computer modeling plays a significant role in the nanocluster research and helps to optimize
the operating conditions to create nanoclusters with a desired size distribution and properties. Commonly known computational methods such as molecular dynamics and Monte Carlo simulation are used for modelling and prediction of effects of experimental conditions on PSD \cite{17,18} However, Monte Carlo simulations are limited to a rather small number of atoms in clusters due to significant computational requirements. In Chapter 4 a mean-field description of PSD evolution via cluster coagulation driven by Brownian motion in the aggregation chamber is presented. The population balance equations for the cluster size distribution are based on the Smoluchowski coagulation equation and take into account (i) convective diffusion of clusters, (ii) cluster loss to walls of an aggregation chamber and (iii) formation of fractal-like aggregates. An efficient numerical technique for solving population balance equation is formulated.

Chapter 5 is devoted to study the Cu nanocluster formation by the gas aggregation technique in the experimental setup as described in Chapter 2. First, a series of experiments was carried out to explore the capabilities of the setup. Then, more detailed experiments were performed to study kinetics of cluster formation inside the aggregation chamber with two types of gas, Ar and Kr, and at two different pressures, 20 and 40 Pa. The morphology and the size distribution of produced nanoclusters were characterized with transmission electron microscopy (TEM) and image analysis technique. The experimental data are compared to simulation results obtained with the kinetic model developed in Chapter 4.

In Chapter 6 the kinetics of the formation of silica fractal-like aggregates during combustion of a stoichiometric methane/air mixture with the hexamethyldisiloxane admixture is presented. At a sufficiently high concentration of hexamethyldisiloxane random collisions of silica nanoparticles lead to agglomerates with a fractal-like structure. TEM is combined with the theoretical analysis to find conditions for the formation of silica fractal-like aggregates. The onset of fractal-like aggregate formation is discussed by studying the characteristic time scales of collisions and coalescence. A model is formulated to describe the evolution of the size distribution of fractal-like silica particles undergoing generation, convection, sintering and Smoluchowski coagulation. The simulation results are compared with experimental data. The study of silica nanoparticles is motivated by a growing interest to biogas as a renewable resource of energy. Biogas has a potential impact to replace about 20–30% of the total natural gas consumption, see e.g. \cite{19}. Biogas is produced naturally during the anaerobic degradation of organic material in landfills, waste water treatment plants and biowaste digesters. Biogas main components are methane (up to 70%), carbon dioxide, nitrogen and oxygen \cite{20}. Before usage in energy generating equipments or the injection into natural gas grid, biogas has to be
upgraded and cleaned from contaminations. In general, trace compounds present in biogas can affect fuel-to-energy processing equipment, especially when processing involves sophisticated techniques such as catalytic reactors [21]. Depending on source, biogas contains varying quantities of contaminations such as halogenated compounds, sulphur compounds and volatile organic compounds, including organic silicon compounds [20–24]. The most common organic silicon impurities are siloxanes which are widely used in industrial and consumer products. In waste water digesters and landfills, siloxanes volatilize into biogas. Physical properties of volatile cyclic and linear siloxanes commonly found in biogas are listed in [25–27].

In particular siloxanes in biogas need special attention. When using biogas as an energy source, during combustion, all types of siloxanes are converted into silicon dioxide particles which deposit onto internal parts of the equipment [23,26,27]. According to Urban et al [28] the concentration of hexamethyldisiloxane (C₆H₁₈Si₂O, denoted as L2) in landfill gas can reach values as high as 1449 mg/m³ or 200 ppmv (in the following ppmv ≡ ppm). Current technologies for siloxanes removal from biogas are reviewed in [26,29,30]. When biogas is injected into natural gas grids the impurities become diluted. However, at the moment there is no generally accepted requirement for limiting siloxane concentration in biogas. Siloxane limits from several manufacturers are listed in [27]. For example, Capstone Turbine Corporation producing microturbine systems has experienced siloxane-induced turbine failures at multiple sites. As a result, Capstone fuel specification requires less than 5 ppbv (~ 0.03 mg/m³) of siloxane [27].

According to reference [31] devoted to challenges and aims of a European standard on biomethane for grid injection and use as a fuel, in the European countries no regular studies have been carried out in order to define precisely a threshold of siloxanes in biomethane. The only exceptions are Austria and the Netherlands where the siloxane specification are 10 mgSi/m³n and 5 ppm respectively [31]. Because of the growing trend towards the introduction of biogases in the natural gas grid the development of well-grounded siloxane/silicon specifications for gas utilization equipment are needed. To develop specifications based on a physically correct basis, fundamental knowledge on silica particle formation in flames and deposition in appliances is essential.

As a practical example in Chapter 7 we consider silica deposition in a typical domestic boiler Intergas Kombi Kompakt HR 28/24 during combustion of siloxane-containing gas as a model system of biogas. This boiler has compact heat exchangers (HE) with narrow channels, which can be relatively easily blocked. It seems that appliances of this type will be particularly susceptible to clogging due to silica deposition. In Chapter 7 we present experimental results on silica deposition
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onto the heat exchanger during combustion of siloxane-containing methane. A model description of silica deposition is developed in order to demonstrate that the mass flux of silica to heat exchanger surfaces is not sensitive to particle coagulation process and particle size distribution. It is shown that the deposition flux of silica depends linearly on siloxane concentration in input air/gas mixture. Thermophoretic transport of silica nanoparticles is considered in the approximation of a laminar boundary-layer flow along a flat isothermal surface. It is shown that the deposition flux depends linearly on total silica concentration close to the burner (or, equivalently, on siloxane concentration in input air/gas mixture). This means that the clogging effect is linear in siloxane concentration, and even trace amounts of siloxanes during prolonged operation of equipments can result in a decrease of thermal performance and premature equipment failure due to clogging by silica particles.

In conclusion: this PhD thesis project has been devoted to nanoparticle formation in the gas phase; both experimental and theoretical methods have been used to investigate the influence of experimental conditions on nanoparticles morphology and size distribution; a number of new results and technique – experimental and theoretical – have resulted from this PhD studies.

1.1 References