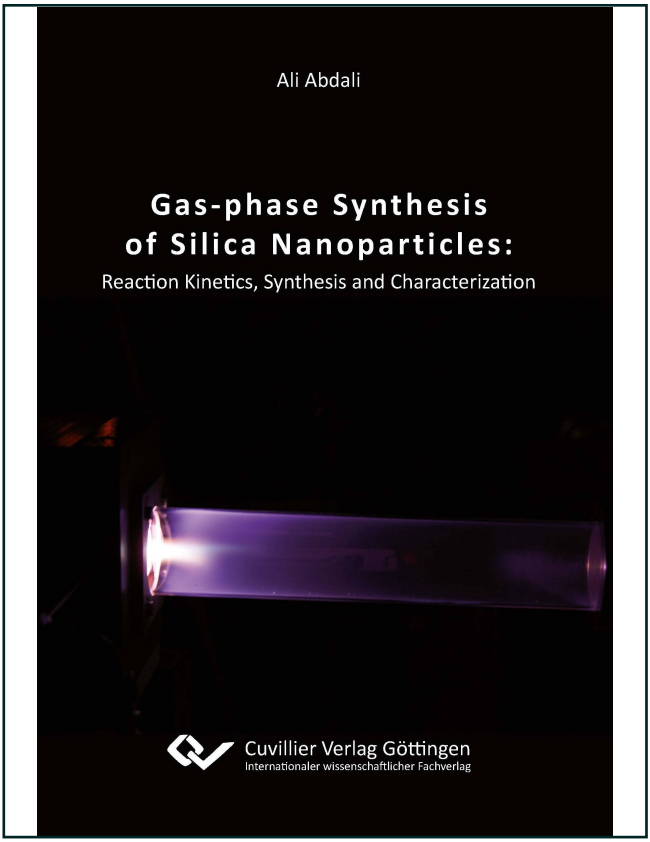
Ali Abdali (Autor)

Gas-phase Synthesis of Silica Nanoparticles: Reaction Kinetics, Synthesis and Characterization



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1. Introduction

Nanotechnology is proving to play a vital role in many disciplines and can be considered the key of future technologies due to the novel properties of materials in the nanosize range, between 1–100 nm. Nanoparticles are viewed by many as fundamental building blocks of nanotechnology. They are the starting point for many 'bottom-up' approaches for preparing nanostructured materials and devices. As such, their synthesis is an important component of rapidly growing research efforts in nanoscale science and engineering [1]. Nanomaterials and ultrathin functional coatings of nanoparticles will determine the utility of many future products such as super-hard materials [2], super fast computers, dirt-repellent surfaces, new cancer treatments, scratch proof coatings and environmentally friendly fuel cells with highly effective catalysts [3, 4]. The properties of materials change as their size approaches the nanoscale and as the percentage of atoms at the surface of a material become significant. It is often observed that the physical (e.g. melting point, conductivity, magnetism) and chemical (e.g. catalytic activity) properties of nanomaterials change depending on the particle size [5]. Most of the worldwide production of nanomaterials on an industrial scale can be assigned to carbon black, silica and titania. Silica nanoparticles have a large range of practical applications. They are widely used as fillers in plastics and coatings to improve material properties such as hardness, tensile strength, abrasion resistance and thermal stability. In particular, applications with demands for high transparency require silica particles with a specific size, morphology, and surface coating [4, 6]. Recent discoveries have reported the use of silica nanoparticles in biotechnology for bio-sensing and drug delivery [7, 8].

Moreover, besides the particle size the quality of the particles such as the particle size distribution and agglomeration index also play an important role on the material properties. Therefore, synthesis of highly defined nanoparticles with specific particle size, size distribution and morphology is desired. Particle agglomeration that commences in the end region of gas phase reactors is an important quality index for a number of applications. For example, agglomerated nanostructured particles are needed for the manufacture of fillers and catalysts [9]. However, if particle agglomeration could be avoided, several advantages could be achieved [10, 11]. Non-agglomerated nanoparticles are essential for many applications such as pigments, nanocomposites e.g. batteries for higher capacity, porous electrodes for energy storage and electronics [9, 12].

Highly specified nanoparticles that have a low agglomeration index and narrow particle size distribution are usually produced using wet-chemistry. However, wet-chemistry requires several processing steps in addition to batch processing and this reduces the production rate and increases the price [13]. Furthermore, these particles may contain impurities from syn-

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thesis and post-processing [14]. Gas-phase synthesis has the advantages of allowing continuous production of pure nanoparticles, easy processing control and possibility to be scaled up from laboratory to industrial scale reactors [15, 16]. The two main disadvantages of gas-phase synthesized particles, especially in conventional large-scale production, is the broad size distribution which is due to the inhomogeneous flow conditions, and the large degree of end-product aggregation that is mainly due to the low cooling rates of the product [17].

It has been found that fast cooling in gas phase reactors enables non-agglomerated nanoparticles, with a narrow particle size distribution, to be produced [6]. Based on this concept a novel gas-phase reactor was built for mass production of highly specified metal-oxide nanoparticles within the scope of the project "Gas-dynamically induced particle synthesis", funded by the German Research Foundation (DFG). The key of this novel process is to provide one-dimensional conditions in the reactor for particle growth with nearly instantaneous decomposition of the precursor, an adjustable time for particle growth and high cooling rates of $-dT/dt = 10^7$ K/s in order to suppress agglomeration [18]. The realization of this concept required several studies such as numerical simulation of the particle formation and growth with integrated reaction kinetics of the precursor [19]. The simulations required detailed experimental data of the precursor decomposition, particle formation and particle growth kinetics which were carried out as part of the work in this thesis.

The primary aim of this work was to investigate the influence of the precursor chemistry on the particle size, size distribution and morphology of the final product. It has been found that the decomposition of a precursor at high temperatures has a negligible influence on the final product [20]. This is due to the very short time scales of the precursor chemistry at the relevant temperature compared to the time required for particle formation and growth. On the other hand, the molecular structure of the monomer that is produced from the precursor decomposition can strongly influence the mechanism of particle formation and growth. In this content, two different silicon containing metalorganic precursors with different molecular structures were chosen for investigation. Tetraethoxysilane (TEOS) and Hexamethyldisiloxane (HMDSO) as halide-free and inexpensive precursor materials are subject to growing interest for particle formation as well as for Chemical Vapor Deposition (CVD) from the gas phase. In this work the precursor chemistry as well as the particle formation were individually studied and the outcome from both studies were then compared. Furthermore, the results of this work provided essential data for the CFD-simulations and construction of the reactor for the Gas-dynamically Induced Particle or so called "GIP reactor".

In this thesis the gas-phase kinetics of TEOS and HMDSO decomposition were investigated in shock tube facilities due to their capacity to instantaneously heat a gas mixture within a wide range of temperatures and pressures that cannot be obtained in other types of testing facili-

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ties. The objective of the shock tube experiments was to study the kinetics of the precursor decomposition and oxidation at high temperatures. The thermal decomposition of TEOS and HMDSO was achieved by combining the shock tube with a time-of-flight mass-spectrometer (TOF-MS). This system was established for the study of complex reaction systems. The fast detection method of high-repetition-rate TOF-MS provides time resolved information about the change in composition of the investigated mixture. Furthermore, the ignition delay times of TEOS and HMDSO were investigated by measuring the onset of OH*-chemiluminescence behind the reflected shockwave in shock tube experiments. Because gas-phase synthesis for nanoparticle formation is often based on flame-synthesis that contains high moisture levels in the flame off-gas, the ignition delay times of TEOS and HMDSO have been investigated in dry as well as moist synthetic air.

Since the focus of these experiments was to investigate the formation and growth of silica nanoparticles, a microwave-supported plasma reactor and a premixed H_2/O_2/Ar-flame reactor were chosen. These two reactors can provide high temperatures at the initial reaction step. The experiments were performed at reduced pressure (30 –70 mbar) to stretch the spatial axis for a detailed analysis of particle formation and growth. The particle formation and growth of silica nanoparticles from TEOS and HMDSO were investigated by measuring the particle size, particle size distribution and particle morphology by systematically varying the main reactor parameters such as temperature, precursor concentration and residence time. Several methods were used in this thesis for in-situ and ex-situ particle characterization such as Transmission Electron Microscopy (TEM) and Particle Mass Spectrometry (PMS).

Due to the lack of information on the microwave-plasma temperature and the influence of the reactor parameters, e.g., reactor pressure and microwave power, the multiline NO-LIF thermometry technique was applied to measure the gas temperature under different conditions. The data from these measurements can support better understanding and interpretation of particle formation and growth in the microwave-plasma reactor.

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2. State of the art

Silicon (Si) is one of the most abundant elements in the Earth's crust, second only to oxygen. In nature silicon is combined with oxygen, in the form of silicon dioxide which is commonly referred to as silica and silicate. Silica is one of the most important silicon compounds occurring in nature as sand and quartz [21]. Bulk silica is used primarily in the production of glass, fused quartz and crystal. Today, through the revolution of nanotechnology, silica nanoparticles are considered an important material for a wide range of practical applications such as additives in plastic and rubber to improve their mechanical properties. Rubber toughening [22] and scratch resistance of polymer coating [23] are some examples. For environmental applications silica nanoparticles have been used as an additive in concrete to reduce the cement content in concrete mixtures [24]. More recently, mesoporous silica nanoparticles (MSN) have gained attention for their potential as controlled release systems and vehicles for the delivery of chemotherapeutics due to their high surface areas, large cavity volumes, and ability to be functionalized with biomolecules for the targeting of specific tissue populations [25, 26]. Such sensitive applications require particles of highly specific size, morphology and surface characteristics. In order to design a new reactor and to control the particle properties, it is essential to understand the detailed precursor kinetics as well as the mechanism of formation and growth of these nanoparticles.

Nanoparticles are generally produced using one of the two so-called “bottom-up” synthesis methods in industry. The first method is liquid-phase synthesis where chemical reactions are applied to solvents. This leads to a colloid, in which the resulting nanoparticles can be stabilized against aggregation by surfactants or ligands. Reviews in this area have been presented by Grieve et al. [27], Trindade et al. [28], and Murray et al. [29]. The second method is gas-phase synthesis which is the subject of this thesis. Gas-phase processes for particle synthesis are usually continuous processes, while liquid-based synthesis processes are often performed in a batch form. Moreover, gas-phase processes are generally purer than liquid-based processes since even the most ultra-pure water contains traces of minerals, detrimental to electronic grade semiconductors [16]. Flame processes are by far the most widely used ones for the manufacture of commercial quantities of nanoparticles. The most important products today are carbon black (Cabot, Columbia), fumed silica (Cabot, EVONIK), pigmentary titania (DuPont, Kerr-McGee) and optical fibers (Heraeus, Sumitomo) [30]. Nonetheless, a scientific understanding of gas-phase synthesis of particles remains a major challenge even though a variety of scientific communities have studied it closely. Swihart [31] critically reviews the state of the art in vapor synthesis of materials, focusing on methods and processes. Strobel et al. [32] review how flame aerosol technology can be used to make various sophisticated materials for sensors, biomaterials, electroceramics, and even nutri-

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tional supplements. Biskos and colleagues [33] review aerosol generation and characterization methods for nanoparticles. Athanassiou and colleagues [34] show how ceramics and even metals are made in scalable flame aerosol reactors.

Fumed silica is the third largest industrial aerosol commodity by value and the fourth largest by volume [35]. The dominant route for synthesis of fumed SiO_2 relies on the oxychloride process for oxidizing various silica precursors, especially $SiCl_4$. Recently, the interest for tetraethoxysilane (TEOS) and hexamethyldisiloxane (HMDSO) as halide-free and inexpensive materials is growing for gas-phase production of silica. Many experimental and theoretical papers have been involved with the thermal decomposition of TEOS in inert conditions. Herzler et al. [36] investigated the thermal decomposition of TEOS in a heated single-pulse shock tube and analyzed the reactants and final stable products. The distribution of gaseous products was monitored by gas chromatography, and the main gaseous stable by-products were found to be ethylene and ethanol. The only source of thermochemical data for TEOS originates from Kee et al. [37] who calculated species enthalpies of some silicon-based species. In the same manner, Kraft and co-workers [38-40] generated thermochemical data for TEOS. Recently, Kraft proposed a reduced kinetics model and particle inception pathways for the flame synthesis of silica nanoparticles from TEOS. They show that the main product of TEOS decomposition is silicic acid ($Si(OH)_4$), which forms silica nanoparticles by condensation reactions [38]. Chu et al. [41] also studied the thermal decomposition of TEOS in a static system with species detection by Fourier-transform infrared spectroscopy (FTIR) in the temperature range between 700 and 820 K. The main by-product they found was ethanol and the decomposition could be described assuming a six-ring elimination mechanism. Takeuchi et al. [42] studied the thermal decomposition of TEOS in a low-pressure CVD reactor at 13 Pa and 950 K. Reaction products as well as the rate of film growth were determined and fitted with a new model. This model quantitatively accounts in the first step for the ethylene formation and the condensation of silanol with TEOS, which finally leads to the formation of ethanol as a stable by-product. Chagger et al. [43] were first to investigate HMDSO combustion in opposed diffusion flames and proposed a reaction mechanism for the formation of SiO_2. Despite the intensive use of this precursor in industry for materials synthesis, there is few or no information about the kinetics and thermochemistry of HMDSO. Wavhal et al. [44] have studied the gas-phase species of HMDSO decomposition in a plasma using optical emission spectroscopy, whereas Carles et al. [45] used a movable mass spectrometer. The production of both, ionized and neutral fragments, occurs through charge transfer between the Ar^+ ion and HMDSO that can be followed by subsequent ion-molecule reactions and the dissociative recombination of the fragment ions. Carles et al. [45] measured the absolute rate coefficients for the dissociative recombination of hexamethyldisiloxane (HMDSO) and pentamethyldisiloxane (PMDSO) cations with electrons. Their results show also several Si-

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containing molecules produced from HMDSO decomposition such as CH_3SiH_2, $(CH_3)_2SiH$ and $(CH_3)_3Si$. Recently, Burkert et al. [46] detected the emission of several excited species such as OH*, CH*, Si* and SiO* of a rich HMDSO/propane/air flame. They have concluded that up to heights of 10 and 40 mm, Si and SiO can be detected, respectively.

Various studies have been conducted on the synthesis of silica nanoparticles from the gas phase using different methods. Ulrich and his co-workers [47, 48] conducted some of the earliest work on the characterization of silica particle formation in flames. Their work focused on the agglomeration processes following the formation of silica particles. Using silicon tetrachloride as the silicon source in a variety of burner configurations, their work suggested that nucleation and surface growth effects were not crucial for controlling the final particle size. Particle growth was governed by coagulation effects. More recently Ahn et al. [49] and Jang [50] have investigated the synthesis of silica nanoparticles from TEOS in diffusion flames, while Goortani et al. [51] have worked on the formation of SiO_2 nanoparticles from quartz in an RF-plasma reactor. They all found that, depending on temperature and precursor concentration, silica nanoparticles with different morphologies and sizes arise along the reaction coordinate ranging from spherical, spatially separated particles to large agglomerates and aggregates. Abdali et al. [52] studied silica particle formation in a microwave plasma reactor using gaseous TEOS as a precursor. They used a hot-wall furnace to extend the residence time in the high temperature region. Their results indicate that the silica particles are disperse in the gas phase, whereas the same particles start to aggregate in the filter downstream of the reactor. They suspect that this is due to the high number of hydroxyl-groups on the particles' surfaces. In the same microwave-plasma reactor Hecht et al. [53] measured the gas temperature distribution in the plasma using multi-line NO-LIF thermometry.

Zachariah and Semerjian [54] found that the choice of precursor affects the mechanism of particle formation and growth. They carried out *in situ* light scattering dissymmetry measurements of the particle size and number density in a counter-propagating non-premixed flame with silane and HMDSO as precursor. Their experiments showed that particle nucleation sets in earlier when using silane compared to organometallics like HMDSO or TMS (tetramethylsilane) but reaches nearly the same number concentration by coagulation further downstream. Briesen et al. [55] studied the effect of the silicon precursor source concentration and oxidant composition on the specific surface area of nanostructured silica particles produced in a non-premixed and premixed $CH_4/O_2/N_2$ flame reactor. For these experiments, hexamethyldisiloxane (HMDSO), octamethylcyclotetrasiloxane (OMCTS) and $SiCl_4$ were used. They found that particles generated by oxidation of organometallic compounds tend to have a smaller specific surface area than the ones made from $SiCl_4$ as precursor. This is attributed

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primarily to the increase of the flame temperature by the additional fuel coming from the organometallic compound.

Several studies have shown that the mechanisms of the particle growth depend on the reactor environment and the temperature history. As Ahn et al. have shown, an initially high temperature seems to support the formation of non-agglomerated and spherical particles. Tsantilis and Pratsinis [6] calculated that fast cooling results in soft agglomerates while in systems with low cooling rates hard agglomerates are formed. Kusters and Pratsinis [1] showed that an increase in the operation temperature generally increases the reaction rate but decreases the surface tension. This provided an excellent way to improve monodispersity. However, they also showed that a high reaction rate and a low surface tension resulted in larger aerosol concentrations and smaller particle sizes. Xiong et al. [56] showed, in theory, that electrical charges during the gas-phase particle generation process reduce the average particle size and narrow the size distribution of particles. Furthermore, Schiel et al. [57] and Reuter et al. [58] studied the influence of the hot-wall temperature on the particle charge, so-called thermionization, and investigated its effect on the particle growth. Their results illustrated that the increase in particle charge that is accompanied with increasing hot-wall temperature hinders particle collisions. Ehrman et al. [59] calculated the characteristic sintering time of silica (for viscous flow) from property data while accounting for the effect of hydroxyl groups. Xiong et al. [60] and Ehrman et al. [59] examined the effects of temperature on the characteristic sintering time of the silica particles. Recently Goertz et al. [61] studied the influence of water vapor concentration on the structural changes of SiO_2 aerosol nanoparticle agglomerates during tempering at a temperature range of 1100–1500 K. They found that the presence of water vapor in the carrier gas strongly accelerated the kinetics.

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