Chapter 2

On the synthesis of nanoparticles

This chapter presents an introduction to different techniques for making and controlling the size of nanoparticles. A detailed description of the two methods that were employed in the thesis project is presented. Section 2.2 explains the synthesis of nanoparticles through the gas aggregation method, design and specifics of the experimental setup. In particular the influence of aging of the target on the deposition efficiency is described. In section 2.3 we discuss the synthesis of nanoparticles in flames. Designs of gas handling system and sampling system are presented.

2.1 Introduction

Materials in the nanometer range were already produced since the 19th century. In 1861 the chemist Thomas Graham created the term colloid to describe a solution containing 1 to 100 nm diameter particles [1]. The first technological uses of nanoparticles were catalysts [2,3] and pigments [4]. The large surface area to volume ratio increases the chemical activity that is advantageous for catalysts. Further research on the production of nanomaterials has been stimulated by these applications; most of them require a defined, narrow size distribution of particles [5]. Currently, the processing capabilities for specially designed nanomaterials have increased considerably to produce the desired shapes, compositions and monodisperse size distributions [6].

Methods for the synthesis of nanoparticles are often grouped into two main types (Fig. 2.1): bottom-up and top-down approaches [7]. The latter refers to crushing of large objects, resulting in small fragments. Examples are lithographic techniques [8], laser-beam processing [9], and mechanical techniques (machining, grinding, and milling) [10]. In the bottom-up strategy, structures are built up by physical and chemical processes from the bottom approach, i.e. atom by atom,
molecule by molecule or cluster by cluster. Examples of this approach include chemical synthesis [11], laser-induced assembly [12], self-assembly [13] and colloidal aggregation [14]. All nanoparticle synthesis techniques fall into one of the three categories: vapor-phase, solution precipitation, and solid-state processes [15]. The selection of a particular respective process depends on the chemical composition and the desired features specified.

![Diagram of Top-Down and Bottom-Up Methods for Nanoparticles Production](image)

**Figure 2.1. Two types of methods for nanoparticles production: top-down and bottom-up.**

Solid-state synthesis generally involves a heat treatment step (in order to achieve the desired crystal structure), which is followed by milling [16]. Milling is a high-energy process that breaks down large particles to smaller sizes. It has been a popular method to make nanoparticles because of its simplicity, relatively inexpensive equipment, and applicability to essentially all classes of materials. Recent innovations in industry claimed that nanoparticles as small as 30 nm with a narrow size distributions can be produced using milling media of a very small size, i.e., 200 µm [17]. However, this method does not allow a full control of particle shape and have potential downside issues such as particles oxidation and rewelding, contamination from the wear debris of the milling media or the container [6].

Precipitation of a solid from a solution is a common technique for the synthesis of fine particles. The general procedure involves reactions in aqueous or non-
aqueous solutions containing the soluble or suspended salts. The particle size and its
distribution, the amount of crystallinity, the crystal structure, and the degree of
dispersion can be affected by reaction kinetics. Factors influencing the rate of
reactions include the concentration of reactants, the reaction temperature, the pH,
and the sequence in which the source materials are added to the solution [5]. Sol-gel
syntheses (production of a gel from powder-shaped materials) are wet-chemical
processes for producing porous nanomaterials, ceramic nanostructured polymers as
well as oxide nanoparticles [15]. The synthesis takes place under relatively mild
conditions and at low temperatures. In sol-gel processes, material production or
deposition takes place from a liquid sol state, which is converted into a solid gel
state via a sol-gel condensation.

The advantage is that the liquid phase enables highly porous materials to be
produced. Nevertheless, there are a number of drawbacks. The disadvantage of the
wet-chemical synthesis of nanomaterials is that often the desired crystalline shapes
cannot be configured and that the thermal stability of the product powder is lower.
This requires a thermal post-treatment with repeated reduction of the particle
surface. Another problem is that undesirable agglomeration at any stage of the
synthesis process can change the properties.

Another technique is the synthesis of nanoparticles from the gas phase by
producing a vapor of the product material using chemical or physical means. The
production of the initial nanoparticles takes place via nucleation. Depending on the
process, further particle growth involves condensation, chemical reaction on the
particle surface or coagulation processes, as well as coalescence processes.

Gas-phase synthesis methods, namely gas aggregation and flame synthesis are
used in this work and will be described in detail in the following sections. At first
glance they might appear very dissimilar, e.g. because of differences in (i)
temperature (more than 1500 K), (ii) source of clustering material (magnetron
sputtering versus combustion) and (iii) pressure (~1 mbar in the aggregation
chamber and ~1 bar in the flame). However, despite these differences both methods
have the same underlying physical mechanisms. Therefore, as we will show,
formation of cluster distributions in both cases is described by similar theoretical
approaches.

Part of this chapter is based on summary that was also presented by the former
PhD student of our MK group, Siete Koch [18], on the application data from Oxford
Applied Research and also on the MSc thesis project of Pieter Visser [19] executed
in the group of Chemical Engineering at the Institute of Technology and
Management (ITM).
2.2 Cluster source

2.2.1 Gas aggregation technique

Gas aggregation, as a technique for producing nanoparticles, refers to the formation of nanoparticles in the gaseous state, i.e., condensing atoms and molecules from a supersaturated vapor in a noble gas atmosphere. It was invented in 1930 [20-22]. The sizes of nanoparticles produced by this method cover the entire range from dimers to nanoparticles of 100 nm in diameter [5].

Description of the process was given by Granqvist and Buhrman [23] and more recently provided by Ichinose et al. [24]. Basically, a setup for producing nanoparticles from a supersaturated solution consists of a vapor source inside a vacuum chamber containing an inert gas, usually Ar or He. In earlier experiments a resistive filament was used as the vapor source, but since then thermal evaporation [25], sputtering [26], electron beam evaporation, laser ablation [27], spark erosion [28] and flame synthesis [29] have been developed as well. Choice of the vapor source has to be made based on required experimental results: size, morphology, phase structure and composition of deposited clusters [30].

A method of producing nanoparticles directly from a supersaturated vapor has the advantages of being versatile, easy to perform and to analyze the particles. It produces high-purity particles, open and closed films on substrates and coatings. However, the disadvantage is that the cost per gram of produced material is still very high [5]. It is also difficult to produce as large a variety of materials and microstructures as one can produce by chemical methods.

In our experimental setup the supersaturation is achieved directly by sputtering the target material with a magnetron discharge and using high pressure of the inert gas. The reason for using a high pressure of an inert gas is that the frequent collisions with the gas atoms decrease the diffusion rate of atoms away from the source region. If the diffusion rate is not limited sufficiently, then supersaturation is not achieved and individual atoms or very small clusters are formed. Usually an inert gas is used to limit the diffusion by shortening the mean free path. However, mixtures of an inert gas and another gas that reacts with the sputtered atoms have also been used to produce molecular nanoparticles. As expected the atomic mass of the inert gas has an influence on the formation of clusters. The heavier inert gas atoms, the more effectively they decrease the mean free path. It has been showed that the cluster size increases when going from He to Ar up to Xe [23].

Nucleation from a supersaturated vapor phase occurs when vapor molecules condense to form small droplets or nuclei. There are two kinds of nucleation [6]:
homogeneous and heterogeneous. In homogeneous nucleation, nuclei are formed in a completely uniform environment. In heterogeneous nucleation, nuclei are preferentially formed onto some other supporting media such as existing particles or the walls of the container. In the case of gas aggregation technique, where particles are formed directly from the vapor, it is usually assumed that a considerable fraction occurs via homogeneous nucleation [5].

After stable nuclei are formed, nanoparticles may grow. Concentration and size distribution of formed clusters depends on number of parameters such as residence time in the aggregation region, gas temperature, and densities of the precursor and the inert gas. As cluster growth cannot be studied in detail during experiments, a convenient way to learn about the influence of these parameters is by computer simulation. A detailed model of cluster formation process is presented in Chapter 4. It considers nucleation and cluster growth from a supersaturated atomic vapor in a buffer gas. In Chapter 5 we study the cluster formation process experimentally and compare obtained results with model predictions. A schematic overview of the experimental setup using gas aggregation technique to produce nanoparticles is given in Fig. 2.2.

Figure 2.2. Schematic overview of the experimental setup used in this work: 1 – process gas inlets, 2 – magnetron power supply, 3 – cooling water, 4 – pressure gauges, 5 – aggregation length 50-200 mm, 6 – aggregation chamber, 7 – aperture, 8 – TMP and scroll pumps, 9 – sample holder, 10 – deposition chamber, 11 – gate valve, 12 – saddle field fast atom bombardment gun, 13 – mechanical transporter, 14 – TMP and diaphragm pump, 15 – airlock. The NC200-UHV nanocluster source is depicted in blue color.

2.2.2 The NC200-UHV source of nanoclusters

An instrument utilized for producing nanoclusters was a NC200-UHV nanocluster source manufactured by Oxford Applied Research (Fig. 2.3). It is designed to produce beams of well-defined nanoparticles using the gas aggregation method. The material is sputtered from a standard 50 mm target by a DC magnetron source into the high pressure aggregation region. The clusters are formed in this region and then transferred through aperture into the deposition chamber.
The cluster size can be varied by adjusting the following parameters: power supplied to the magnetron, the aperture size, the gas flow rate, type of gas, temperature in the aggregation region and distance between the magnetron and the aperture (aggregation length). Due to the nature of the gas aggregation technique, narrow size distributions can be achieved without the need for further mass-selection.

Figure 2.3. External view of the NC200-UHV cluster source with installed copper target.

The source is capable of producing clusters consisting of a couple of tens of atoms up to particles with diameters of more than 20 nm for a large number of materials including semiconductors, magnetic materials and most metals (Fig. 2.4). Compound clusters, such as TiO$_2$, can also be formed by adding O$_2$ to the aggregation region during operation.

Figure 2.4. Materials that can be used as targets in the NC200-UHV nanocluster source are highlighted in blue.
A large percentage of the clusters generated by the source are ionized (typically 40% for Cu clusters). An ionized beam can be accelerated towards a substrate. This technique is called energetic cluster impact [31]. It can be used to form highly adherent and uniform coatings. The ionized clusters can also be electrostatically manipulated in the deposition system. The mass of the ionized clusters can be measured and filtered by devices such as quadrupole mass filter [32] if necessary to achieve even more narrow size distribution.

The NC200-UHV source is capable of depositing at rates between $< 0.001$ nm/s and $> 0.5$ nm/s (measured at a distance of 100 mm for Cu clusters). The deposition rate achieved depends on a number of parameters which includes the material and the size of clusters required.

The experimental setup is designed to accommodate different magnetron sputtering guns, for example MicroMagnetics SpinTron, which is available in the MK lab and can be mounted using an adapter flange. The SpinTron can be used with RF power supply. This allows sputtering of insulating targets much more efficiently than in case of DC power supply.

### 2.2.3 Magnetron sputtering

The magnetron sputtering device has been designed specifically for high operating pressure of up to 1 mbar and for a high sputtering rate. This design concept is licensed from Haberland, who first applied the sputter discharge technique in a cluster source instead of the conventional thermal evaporation [33]. DC voltage in the range of 100-500 V is applied between the target (cathode) and the magnetron cover (anode). The separation between these components is adjustable and typically amounts to 0.2-0.5 mm depending on the target material. Small separations are required for magnetic materials.

An inert gas is floated directly over the sputter target. Due to the potential difference, electrons are accelerated away from the cathode and collide with the gas atoms, giving rise to excitations. The latter can decay to lower energy levels by the emission of light, thus forming the characteristic glow discharge. A part of Ar atoms is ionized in collisions with the energetic electrons, then they are accelerated towards the target, and release secondary electrons upon impact. The secondary electrons are repelled from the cathode and they feed the ionization process further, making this a more or less self-sustaining process. In addition, the discharge ions sputter atoms from the target as the precursor for the clustering process.

A disadvantage of using a magnetron sputtering device is the difficulty encountered when sputtering magnetic targets. The effect of the magnetic field is reduced, leading to under-utilization of the target material and weak sputtering.
Depending on the magnetic saturation of the material, the thickness of the target needs to be limited to a level that still enables a sufficient magnetic field to be projected on the target surface. This amounts to 1-2 mm for Fe targets and 3-4 mm for Co targets. Obviously a thinner target requires more frequent replacement.

2.2.4 Aggregation chamber

As was mentioned earlier, the cluster formation takes place in the aggregation chamber. Here, the gas pressure is measured by a wide-range gauge connected to one of the three gas inlets of the cluster source. The other two inlets (Fig. 2.3) are intended to be used for sputter and drift gases. In our setup the gas flow rate is controlled and measured by a digital mass flow controller (MKS MF1). The base pressure measured in the aggregation chamber is \(10^{-6}\) mbar; it increases to about \(10^{-1}\) mbar when the gas is introduced.

The aggregation process has to be stopped before the clusters become too large. This is done by letting the inert gas transport the clusters through an aperture where the growth effectively comes to an end. The aperture of different size can be installed. In this work we used apertures of 1 and 3 mm in diameter. A larger opening means faster gas effusion, resulting in a shorter residence time of clusters in the aggregation chamber and consequently smaller clusters. Distance between the magnetron and the aperture can be adjusted by means of a linear motion drive. This allows one to vary the residence time of clusters, hence, the cluster size. The available length range is 50 to 200 mm.

The cluster source is operated with cooling water at temperature of \(\sim 15\, ^\circ\text{C}\) which flows inside the walls of the aggregation tube. Alternatively, liquid nitrogen can be used for cooling to stabilize the beam and make the operating conditions more tolerant [34]. Previous experiments with this cluster source showed that cooling with water also yields good results [18].

Effects of experimental parameters such as deposition time, aggregation length, pressure in the aggregation chamber, aperture size and type of the inert gas on the cluster size, morphology and concentration are discussed in Chapter 5.

2.2.5 Deposition chamber

After passing through the aperture, clusters enter the deposition chamber where the substrate is located. The gas is pumped by a 1300 l/s turbomolecular pump (BOC Edwards STP-A1303C), backed up by a scroll vacuum pump (BOC Edwards XDS35i). As a result, a base pressure of about \(10^{-7}\) mbar is established. During deposition the pressure increases up to \(10^{-4}\) mbar. A sample holder has 5 positions
for standard 3 mm TEM grids that can be used for simultaneous deposition. The holder is mounted on a stage that has 4 degrees of freedom. It can be moved in three directions, as well as rotated along one axis. The stage can be heated up to 300 °C giving a possibility to study the cluster deposition process at elevated temperatures of the substrate. The stage is electrically insulated from the ground, therefore a potential can be applied to the substrate in order to attract or repel charged particles.

An electron beam evaporator and a thermal evaporator are installed in the deposition chamber. Although both are used for the same purpose of physical vapor deposition, they have its own advantages and disadvantages. A detailed review of these techniques is presented in the literature [35,36]. The evaporators can be utilized for coating of the substrates with a thin film. Another application is the production of nanocomposite materials [37] by using the evaporator simultaneously with the cluster source.

The intermediate chamber is located next to the deposition chamber and separated from it by a gate valve. This chamber has a separate pumping system comprised of a turbomolecular pump (BOC Edwards EXT250) and a diaphragm pump (Pfeiffer MVP035-2). Vacuum levels in both deposition and intermediate chambers are registered by Pirani and Penning gauges. Such combination enables us to measure a wide range of pressures starting from atmospheric and down to $10^{-9}$ mbar. The intermediate chamber contains a saddle field fast atom bombardment gun that could be used for cleaning the substrate before deposition [38]. Ion current from the gun is measured by a Faraday cup [39].

Samples are introduced into the experimental setup by means of a mechanical transporter. To preserve vacuum in the whole system an airlock is used when transferring samples. Similar to the intermediate chamber, the airlock is evacuated by a separate pumping system. Samples are changed quickly with such a design. For the purpose of venting, nitrogen can be introduced via a system of needle valves into every chamber of the vacuum system. It is important to note that all vacuum pumps of the experimental setup are oil-free. This approach reduces contamination of the vacuum system and, as a result, improves quality of experiments. The overview of the experimental setup is presented in Fig. 2.5.

The deposition process is designed to run fully automatic. A computer based system uses in-house written LabVIEW software for experiment control and data acquisition. In order to start a deposition, user needs to input few parameters, particularly, gas flow rate, process current (or voltage) and deposition time. The hardware used to control the experimental setup and the image of the computer screen during the deposition process are shown in Fig. 2.6.
Figure 2.5. The home-made experimental setup for producing nanoclusters using gas aggregation technique.

Figure 2.6. Hardware used to control the experimental setup (left) and home-made software displayed during the deposition process (right).
During the experiments the values of all controlling parameters are saved automatically to a log-file for further analysis. Process control includes several safety functions. The software monitors pressure in different chambers, the magnetron power supply and the gas flow rate. If one of the parameters goes beyond the defined tolerance, the software will halt the deposition process. More precisely, the software will switch off the power supply to the magnetron and stop the gas flow, in fact bringing the system in a standby mode. This makes the setup safer and, in principle, allows one running it unattended, what is especially convenient for long-time experiments.

2.2.6 Influence of target aging on deposition efficiency

Non-uniform erosion of planar targets is one of the disadvantages in conventional magnetron sputtering technique. Inhomogeneous plasma above the target leads to formation of a groove in the target which is typically called the race-track (Fig. 2.7). During magnetron operation the magnetic field strength in the vicinity of the race-track surface will change resulting in slightly altered plasma density and erosion rate [40]. For this reason, the spatial distribution of sputtered particle flux evolves with time.

![Figure 2.7. A new 50 mm plane target (left) and the target used for several hours with the deep race-track (right). Redeposition of sputtered material can be seen on the used target as dark red color.](image)

In our experiments we observed a difference in the deposition efficiency when using a new or eroded target (Fig. 2.8), which can be due to an altered flux distribution. The deposition efficiency in this case is defined as the ratio of the material mass removed from the target to the mass deposited onto the substrate. One can notice rather low efficiency which is only about 1%. There are several reasons
for that, for example usage of a small limiting aperture and diffusion of particles to the chamber walls. These aspects are discussed in detail in Chapter 4 and 5.

![Graph of deposition efficiency](image)

**Figure 2.8.** Deposition efficiency at different aggregation lengths. The used target has a lower efficiency due to formation of the race-track.

To study the rate of target erosion, experiments have been carried out using a new 2 mm thick copper target. The test conditions were as follows: Ar gas flow rate 10 sccm, pressure in the aggregation chamber 40 Pa, magnetron current 0.2 A. In total, 10 experiments of one hour duration have been performed using the same target. After each deposition experiment the target was removed from the magnetron; its surface was measured using the confocal microscopy (Fig. 2.9). Then the target was installed back keeping in the same orientation.

![Confocal microscopy images](image)

**Figure 2.9.** A typical confocal microscopy image used to measure the race-track profile (a). 3D representation of the race-track (b).
Race-track profiles of eroded targets were measured using confocal microscope images. Measurements for each sample are indicated by different symbols in Fig. 2.10. To characterize the erosion profile, a Gaussian fit is commonly used because of its mathematical simplicity [40]. It approximates the measured profiles very well, at least in the interesting regions of the race-track. An example of the fitting of erosion profile after 10 hours of deposition is shown in Fig. 2.10 by the solid black line. Noticeable redeposition of sputtered material occurs on the inner part of the target. As can be seen, the longer the deposition time, the higher becomes the left side of race-track profiles (Fig. 2.10). It is not so evident after 1 hour, but after 10 hours the height of redeposited layer increases to more than 200 µm in the vicinity of the race-track. Redeposition is also partly visible as dark red color on the photo of the used target (Fig. 2.7)

![Figure 2.10. Depth profiles of the eroded copper targets (symbols). The solid line represents the Gaussian fit used to quantify the measured data.](image-url)

Parameters of the race-track profiles such as the depth, the radial position and the peak full width at half maximum (FWHM) were measured for the total of 5 samples (Table 2.1).
Table 2.1. Measured parameters of the race-track profiles.

<table>
<thead>
<tr>
<th>Time, h</th>
<th>Depth, mm</th>
<th>Radial position, mm</th>
<th>FWHM, mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.15</td>
<td>16.45</td>
<td>3.64</td>
</tr>
<tr>
<td>3</td>
<td>0.38</td>
<td>16.39</td>
<td>3.55</td>
</tr>
<tr>
<td>4</td>
<td>0.49</td>
<td>16.37</td>
<td>3.41</td>
</tr>
<tr>
<td>5</td>
<td>0.62</td>
<td>16.32</td>
<td>3.36</td>
</tr>
<tr>
<td>10</td>
<td>1.15</td>
<td>16.18</td>
<td>3.35</td>
</tr>
</tbody>
</table>

The influence of target aging on deposition efficiency is substantial. Experiments have shown 20% reduction of deposition efficiency after 1 hour of deposition. As we mentioned earlier, the main reason is the formation of eroded groove on the target, leading to the change of the spatial distribution of sputtered atom flux. Further measurements showed continuous development of the race-track. To describe the influence of target aging on deposition efficiency a complex study is necessary which would take into account numerous physical processes including the angular dependence of sputtered atoms, the formation of distribution of thermalized precursor atoms in the flowing buffer gas, the nanocluster formation and effusion through the opening in the aggregation chamber. Such a detailed description is beyond the scope of this thesis. In the following we will focus on the processes and parameters controlling formation of nanoparticles inside the aggregation chamber. For our purposes it is sufficient to assume that the concentration profile of sputtered atoms near the target is parabolic in radial direction (see Chapter 4).

2.3 Nanoparticles formation in flames

2.3.1 Formation of silica nanoparticles during combustion of methane/air mixture with the siloxane admixture

Siloxanes are converted into silicon dioxide particles upon combustion. The size, morphology and concentration of formed silica particles depend on many parameters. Among them are the siloxane concentration, flame temperature, distance from the burner, etc. Potential issues of siloxanes presence in biogas are mentioned in Chapter 1. In this section we describe experimental methods used to study the formation of silica nanoparticles.

Experiments on the silica particle formation were performed in laminar premixed flames at well-defined laboratory conditions (at DNV KEMA Gas Consulting & Services Groningen). Siloxane presence in biogas was simulated by
addition of either hexamethyldisiloxane (L2) or decamethylcyclopentasiloxane (D5) to the methane/air mixture. The former has a linear structure with 2 silicon atoms, whereas D5 has cyclic structure and 5 silicon atoms (Fig. 2.11). However, initial tests with D5 addition showed that the concentration of siloxanes is too low even at full saturation and therefore only L2 was used for all further experiments. L2 has much higher vapor pressure; therefore the maximum siloxane concentration can be higher.

![Figure 2.11. Repeating structural units for linear (left) and cyclic (right) siloxanes. The linear and cyclic siloxanes are denoted as L2 and D5, respectively.](image)

Laminar premixed flames are convenient for research due to the relatively simple 1-D structure that can be simulated numerically and compared to experiments [41]. In laminar premixed flames, fuel and oxidizer are homogeneously mixed prior to combustion. The composition of a premixed fuel/oxidizer mixture is usually expressed as the equivalence ratio \( \phi \). A flame is considered stoichiometric (\( \phi = 1 \)) if fuel and oxidizer consume each other completely leaving only reaction products. Fuel rich combustion occurs in the case of excess fuel (\( \phi > 1 \)) and fuel lean combustion occurs in the case of excess oxidizer (\( \phi < 1 \)).

Combustion of L2 in biogases (mainly methane) is a sequential process involving many reactions. There is no well-defined temperature at which silica becomes in the solid state (melting point depending on the structure is about 1990 K [42]). However, we can assume that all silica eventually become solid after cooling down to moderate temperatures (<1500 K). After combustion silicon containing compounds are considered to be in an equilibrium state.

### 2.3.2 Gas handling system and burner

The experimental setup is shown schematically in Fig. 2.12. It consists of two main parts: the gas handling system and the sampling system. The gas handling system is used to create gas mixture of air, methane and siloxane and feed it to a burner. To add L2-siloxane to the gas mixture the methane flow is divided into two
parts. One part goes through a custom made pressure resistant gas bubblers containing L2 and then two parts of fuel are mixed with air [43]. The methane and air gas flows are mixed using a static mixing tube to ensure homogeneous mixing. Methane supplied in gas cylinders, with purity better than 99.99% as guaranteed by manufacturer, was used during the experimental work. The air is dried and made free of particulates and oil on-site using filters. Temperature and pressure in the gas bubblers are measured using a digital thermometer and an analog pressure gauge.

![Diagram](image1.png)

**Figure 2.12. Schematic overview of the experimental setup used to study nanoparticles formation in flames.** P – pressure gauge, F – flow meter, FC – flow controller, T – temperature meter, M – manual valve, R – reducer.

The silica particles and aggregates are produced in a flat flame obtained in a burner with perforated ceramic plate [44] with a diameter of 60 mm and aperture diameter of 1 mm (Fig. 2.13). A cylindrical chimney with a 6 cm inner diameter and a length of 40 cm was positioned above the burner to stabilize the flame.

![Flame](image2.png)

**Figure 2.13. Photograph of the custom made perforated ceramic tile burner with stabilized flat flame.**
2.3.3 Sampling system

Silica particles in the flame at various distances from the burner were sampled by transferring a probe holding 3 mm TEM grid in the flame. The working principle of the sampling system is based on thermophoresis: silica particles are deposited to the grid because of the temperature difference between the hot surrounding gas and the relatively cold grid. The larger the temperature difference between the grid and the surrounding gas molecules, the larger the thermophoretic force applied to the particles.

We have followed the study of Lee et al. [45] to fabricate the thermophoretic probe. Lee et al. reviewed thermophoretic sampling techniques and proposed an improved design for sampling with high spatial resolution. They have shown that probe construction can significantly affect the precision of particle sampling in flame. This approach with modifications described below allowed us to make an efficient probe that minimally disturbs the flame when collecting particles.

![Diagram of the sampling system](image)

**Figure 2.14. Localized home-made thermophoretic sampling system with two nitrogen-driven pneumatic pistons.**

The sampling system consists of computer-controlled positioner, two nitrogen-driven pneumatic pistons and the probe (Fig. 2.14). An electronic circuit capable of producing pulses of duration 50 to 1000 ms controls the solenoid valves used to relay pressure to the pneumatic cylinders. A 100 MHz digital oscilloscope was used to determine the pulse duration that was assumed to be equal to the sampling time. Sampling times were selected so that collected silica aggregates do not overlap. The
TEM grid was covered by a shield to prevent particles from being deposited onto it while the sampling probe is inserted into and withdrawn from the flame. This is necessary because at the outermost areas of the flame a temperature gradient is present which has a large influence on the growth of silica particles. During the sampling process, the first piston moves the TEM grid holder closed by the shield into the flame, and then the second one extends the grid out of the shield to expose the grid for sampling only after the probe is located at the desired position in the flame. The sampling area of the grid was limited by a hole of 2.3 mm in diameter.

The sampling system is designed in such a way, that the probe can be rotated 90° enabling vertical insertion. In this case the TEM grid is oriented parallel to the gas flow (Fig. 2.15c). Results of the experiments for different probe orientations are shown in Figs. 2.15b and 2.15d. During vertical sampling the amount of deposited material decreases because only the thermophoretic effect is operative. The important observation is that collected particles in both cases have similar mean size and morphology. Further discussion of this experiment is presented in Chapter 6.

Figure 2.15. Schematic of different insertion methods and TEM images showing the samples collected during horizontal (upper row) and vertical insertion of the probe (lower row).
Initially we tested two variants in the probe design. The first type probe (Fig. 2.16a) had one opening with a diameter of 2.3 mm and an indent of 3.1 mm from the top for the TEM grid. The distance from the grid to the bottom of the probe is 1 mm. The second type probe (Fig. 2.16d) had two additional 3.1 mm openings on both sides of the grid. The distance from the grid to the bottom of the probe was reduced to 0.2 mm.

Figure 2.16. Drawings of thermophoretic probes (a) and (d) and TEM micrographs showing collected silica aggregates formed at different heights above the burner with L2 concentration 2700 ppm.

Multiple sampling experiments at L2 concentration of 2700 ppm (the L2 concentration is measured in the unburned fuel/air mixture) with the first type of the probe showed neither a considerable morphology nor a concentration difference among measurements at various heights (Figs. 2.16b and 2.16c). In contrast, when sampling with the second probe a substantially higher amount of material was collected (Figs. 2.16e and 2.16f). Based on these measurements all subsequent experiments have been made with the second probe. As can be seen in Figs. 2.16e and 2.16f, the concentration of particles is too high for a quantitative image analysis, therefore a reduced L2 concentration was used for investigation of nanoparticles growth.
2.4 References
