

# Gas-phase synthesis of silica nanoparticles in a hybrid microwave-plasma hot-wall reactor

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## ABSTRACT

The synthesis of silica nanoparticles from tetraethoxysilane (TEOS) was investigated in a combination of a microwave-plasma reactor with a subsequent hot-wall furnace. This combination was used to provide variable temperature/time profiles and therefore to investigate the growth of silica particles in detail. Particle properties such as size, size distribution, shape, morphology, and agglomeration were investigated via transmission electron microscopy (TEM). The samples were collected on TEM grids in-situ from the reactor and ex-situ from a filter device. The particles collected directly from the gas flow in the reactor are non-agglomerated and have a spherical morphology. However, those obtained from the filter are spherical in shape but have a high degree of agglomeration.

**Keywords:** TEOS, silica particles, gas-phase synthesis, plasma reactor

## 1 INTRODUCTION

The synthesis and characterization of silica nanoparticles has received attention in recent years due to their 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 a demand for high transparency require silica particles with a specific size, morphology, and surface coating [1,2]. Therefore, the synthesis of particles with highly defined particle size, size distribution, and morphology is desired. Most of the silica powder is produced by gas-phase processes, most frequently using flame reactors and spray pyrolysis. However, these methods require exact knowledge of the kinetics of precursor decomposition [3,4], particle formation and particle growth. Tetraethoxysilane (TEOS) as a halide free and inexpensive precursor material is subject to growing interest for particle formation from the gas phase. Various studies have been conducted on the synthesis of silica nanoparticles from the gas phase using different methods. Ahn et al. and Jang have investigated the synthesis of silica nanoparticles from tetraethoxysilane (TEOS) in diffusion flames [5,6], while Goortani et al. have worked on the synthesis of SiO<sub>2</sub> nanoparticles from quartz in a RF plasma

reactor [7]. 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. As Ahn et al. have shown, an initially high temperature seems to support the formation of non-agglomerated, spherical particles, and Tsantilis et al. calculated that fast cooling results in soft agglomerates while in systems with low cooling rates hard agglomerates are formed [8]. To investigate the gas-phase synthesis of silica, experiments are usually performed at atmospheric pressure. To stretch the spatial axis for a detailed analysis of particle formation and growth, our experiments were conducted at reduced pressure (30 to 70 mbar). This allows for a highly resolved sampling of materials with different reaction times from the reactor. Because the focus of our experiments is to investigate the formation of non-agglomerated, spherical particles, a microwave-supported plasma reactor that enables for steep temperature gradients was chosen for the experiments. Additionally, it allows for high temperatures in the initial reaction step and enables for varying the gas composition over a large range.

## 2 EXPERIMENTAL

The hybrid reactor which consists of a microwave plasma reactor and a subsequent hot-wall furnace has been constructed for gas-phase synthesis of high purity silica nanoparticles using TEOS as the precursor. A microwave-induced plasma heats the injected gas mixture consisting of gaseous TEOS, O<sub>2</sub>, and Ar within a few microseconds to high temperatures. This initiates precursor decomposition and chemical reactions followed by particle formation. Behind the plasma typically fast cooling is observed. To achieve longer and variable residence times at high temperature we combine the plasma reactor with a hot-wall furnace (see Fig. 1).

In order to obtain reproducible synthesis conditions, the current apparatus allows the control of gas flow rates, gas composition, pressure, and the temperature of the hot-wall furnace. The reactor pressure can be varied between 20 and 1000 mbar using a control valve. The reactor pressure is varied in order to achieve different residence times. Based on the ideal gas law, the residence time is proportional to pressure for a constant gas flow rate and tempera-

ture. The microwave generator in use has a maximum output power of 2 kW and a frequency of 2.45 GHz. In all experiments the power was fixed at 200 W.

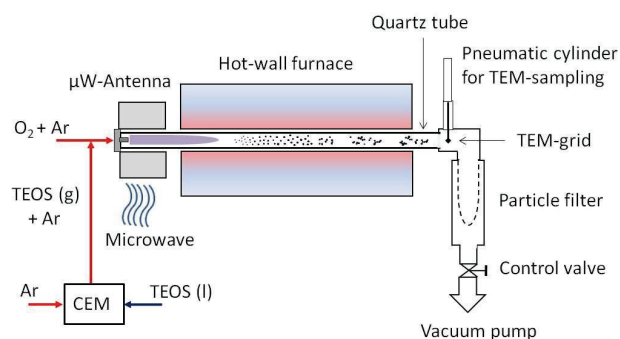


Figure 1: Simplified schematic of the hybrid microwave-plasma hot-wall reactor.

The required gaseous TEOS (in a mixture with Argon as the carrier gas) was supplied using a controlled evaporator mixer (CEM) from Bronkhorst. The CEM system supplies gas mixtures that can feed up to 13 g/h of TEOS vapor into the reactor despite the poor vapor pressure of TEOS (2.0 mbar at 20°C). The tube that connects the CEM and the reactor inlet is heated to 80°C to prevent condensation of TEOS. An additional gas mixture of Argon and Oxygen, as oxidizing reagent, is added to the TEOS/Argon mixture prior to entering the reactor. The purity of the gases used is 99.999% for Argon and Oxygen, and 98% for TEOS.

The particles produced are filtered from the gas using a cellulose extraction thimble. The size, shape, and morphology of the product were analyzed by transmission electron microscopy (TEM) using a Philips CM12 microscope. The TEM samples were either collected from the filter or directly from the reactor chamber by thermophoretic deposition onto TEM grids using a double acting pneumatic cylinder that limits the sampling time to an exactly defined time. For our experiments we used sampling times of 0.5 s.

In addition, material sampled from the filter device was also used for BET analysis (isothermal Brunauer-Emmett-Teller nitrogen adsorption). The primary average BET particle diameter was calculated based on the measured surface area assuming monodisperse and spherical particles. In order to calculate the equivalent diameter, the following equation was used:

$$D = \frac{6 \times 10^6}{\rho \text{ SSA}} \quad (1)$$

where  $\rho$  is the bulk density of silica (2200 kg/m<sup>3</sup>), SSA is the specific surface area in m<sup>2</sup>/g, and  $D$  is the diameter of the nanoparticles in nm.

### 3 RESULTS AND DISCUSSION

The growth of the particles was systematically investigated by changing different parameters which are expected to influence the particle size as well as the particle morphology. The particle size was investigated at furnace temperatures that were varied between 200 and 800°C, whilst keeping the gas flow rates constant (Argon: 2.1 l/min, Oxygen: 1.0 l/min, TEOS: 3 g/h (equivalent to 1700 ppm)). A representative TEM image of silica nanoparticles obtained by thermophoretic sampling from the reactor chamber is shown in figure 2. In all cases the particles were non-agglomerated and had an almost spherical morphology.

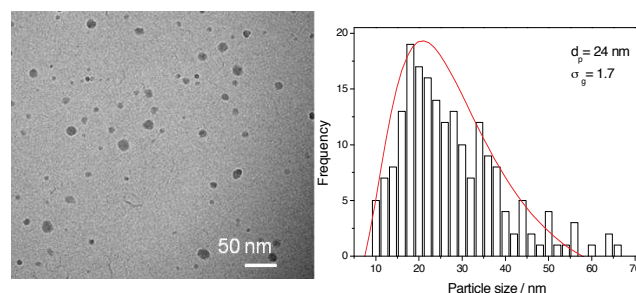


Figure 2: TEM-image of silica nanoparticles sampled from the reactor chamber (left); histogram and fitted log-normal size distribution (right)

The diameter of about 200 silica nanoparticles, observed on the different TEM grids, was measured and used to generate a histogram such as the one shown in figure 2. A log-normal particle size distribution was fitted to the histogram to calculate the mean particle diameter. These values were used to create the graphs that show the dependencies between experimental parameters and particle size (Figs. 3 and 4).

In figure 3 the red profile shows that for furnace temperatures up to 400°C the mean particle size increases as expected, with the maximum particle size of 28 nm. However, the particle sizes decrease when the furnace temperature exceeds 400°C. We attribute this to two reasons: As it is expected from plasma synthesis of nanoparticles, Coulomb repulsion plays an important role in preventing agglomeration and at high furnace temperatures the particles are likely to gain a higher charge, thus hindering particle collisions and growth due to Coulomb repulsion [9]. Thus, further particle growth would be increasingly prevented with increasing the particle charge. Additionally, the residence time decreases with increasing furnace temperature because of the reduced density at fixed pressure and gas flow rate. The influence of decreasing residence times on the particle size at high temperatures was investigated. For different temperatures the reactor pressure was varied in

order to keep the residence time fixed at 164 ms. The results of these tests are shown in figure 3 (black profile). In figure 3 it can be seen that the particle sizes are bigger at the longer residence time of 164 ms. However, the particle size again decreases above furnace temperatures of 400°C due to the Coulomb repulsion.

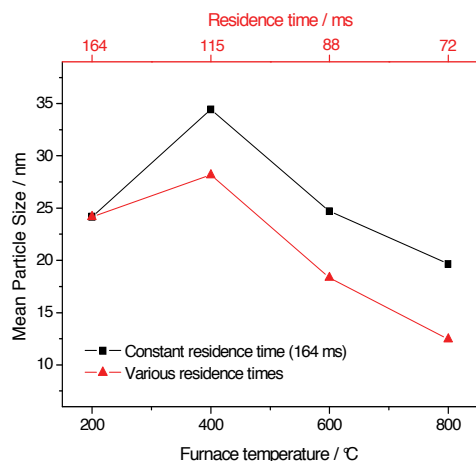


Figure 3: Influence of the furnace temperature on particle size. (▲) various residence times at constant pressure; (■) constant residence time at various pressures

To investigate whether the residence time within the reactor influences the particle growth, the furnace temperature was kept at 800°C whilst the residence time was increased from 72 to 126 ms by raising the reactor pressure from 40 to 70 mbar. As can be seen from figure 4, the mean particle diameter depends very strongly, and almost linearly, on the residence time in this case.

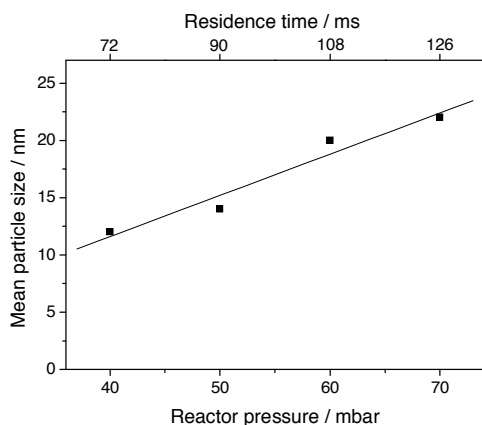


Figure 4: Influence of reactor pressure on the particle size, furnace temperature 800°C.

These results clearly demonstrate that we were able to adjust the size of silica nanoparticles, prepared by gas-phase synthesis, via two independent parameters, namely

the furnace temperature and the residence time in the hot zone of the reactor.

All samples received from the filter or by thermophoretic sampling from the cold walls downstream of the reactor always showed a very high degree of particle agglomeration (see Fig. 5 left). The findings discussed above demonstrate that the particles in the gas phase are well separated (as it was shown earlier in figure 2), while hard agglomerates are found in samples taken from the filter and from the cold reactor walls. The highest agglomeration index was obtained with TEOS concentration of 3700 ppm, reactor pressure of 40 mbar and furnace temperature of 400°C. Nevertheless, the size distribution of the primary silica nanoparticle that form the large aggregates on the filter followed the same log-normal size distribution function as the non-agglomerated particles sampled from the reactor (see Fig. 5 right).

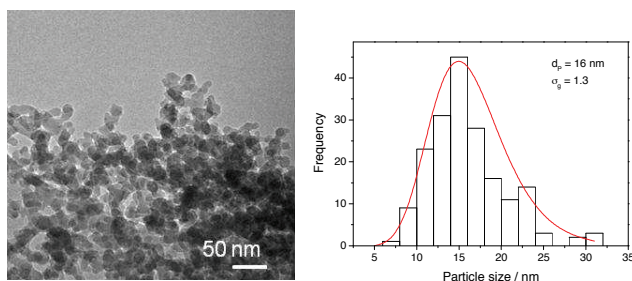


Figure 5: TEM-image of the collected particles from the filter (left); histogram and fitted log-normal size distribution (right)

The BET particle size of the samples from the filter, as shown in figure 5, was 24 nm which is much bigger than that found in the material from the reactor (see Fig. 5 right, mean particle size is 16 nm). The high degree of agglomeration reduces the specific surface area (SSA) and therefore shows larger particle size. The aggregation of formerly spherical, non-agglomerated particles may be attributed to the surface chemistry of the freshly prepared silica nanoparticles. Particle adhesion, especially in the nanosized regime, originates from solid-solid interaction forces (van der Waals forces), capillary bridging, and long-range electrostatic (Coulomb) forces that create strong particle-particle interaction [10]. It is found that materials like inorganic oxides that contain hydroxyl groups on their surface tend to build new, stable chemical bonds in the presence of water [11]. For this reason a particle sample from the filter has been investigated with Fourier Transform Infrared (FTIR) spectroscopy.

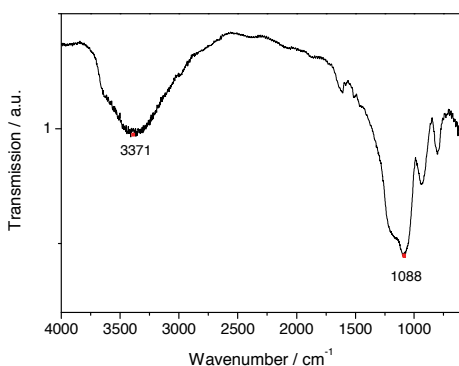


Figure 6: FTIR-Transmission spectrum of SiO<sub>2</sub> nanoparticles.

Figure 6 shows the FTIR spectrum of silica nanoparticles. In the spectrum, a broad peak around 1088 cm<sup>-1</sup> appears, which can be assigned to stretching vibration of Si-O-Si. The peak is broad due to the amorphous nature of silicon oxide. Additionally, the signature from OH vibration around 1700 cm<sup>-1</sup> may be due to some physisorbed water on the nanoparticle surface. The FTIR spectrum also shows a strong signal at about 3371 cm<sup>-1</sup> indicating silanol groups that might be responsible for the highly active particle surface. As a result, we propose that silica nanoparticles that touch each other will sinter together due to condensation of silanol groups on their surface. In this case, temperature and humidity play an important role in the formation of silica aggregates.

## 4 SUMMARY

The gas-phase synthesis of silica nanoparticles was carried out in a hybrid microwave-plasma hot-wall reactor. The particles were collected by thermophoretic deposition on TEM grids directly from within the reactor chamber. TEM analysis reveals that in all cases the particles sampled from the reactor chamber are non-agglomerated, spherical in shape and have a wide size distribution. The influence of the main parameters such as hot-wall furnace temperature and residence time was investigated. The results show that short residence times yield small particles whereas their size increases at longer residence times. In contrast, the analysis of particles from the filter shows large hard agglomerates. When varying the furnace temperature between 200 and 800°C the maximum agglomeration index of the particles sampled in a filter device downstream of the reactor was observed at 400°C. The strong aggregation of the particle powder sampled from the filter is attributed to surface chemistry subsequent to the particle formation process in the gas phase.

## ACKNOWLEDGEMENTS

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