

Hybrid microwave-plasma hot-wall reactor for synthesis of silica nanoparticles under well-controlled conditions

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A microwave-plasma reactor was constructed for gas-phase synthesis of silica nanoparticles from tetraethoxysilane and a subsequent hot-wall furnace was used to enable for different temperature/time profiles. This combination has enabled us 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 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.

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1. Introduction

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 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, 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 SiO₂ 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 performed at reduced pressure (3 to 10 kPa). This allows for a highly resolved sampling of materials out of the reactor. Since the focus of our experiments is to investigate the formation of non-agglomerated, spherical particles, a microwave-supported plasma reactor was chosen for the experiments. It allows for high temperatures at the initial reaction step and allows the gas composition to be varied over a large range.

2. Experimental

A microwave plasma reactor combined with a subsequent hot-wall furnace has been constructed for gas-phase synthesis of high purity silica nanoparticles using TEOS as the precursor. The microwave-induced plasma heats the injected gas mixture, which constitutes gaseous TEOS, O₂ and Ar, within a few microseconds to high temperatures. This initiates the precursor decomposition and the 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 (cf. Fig. 1).

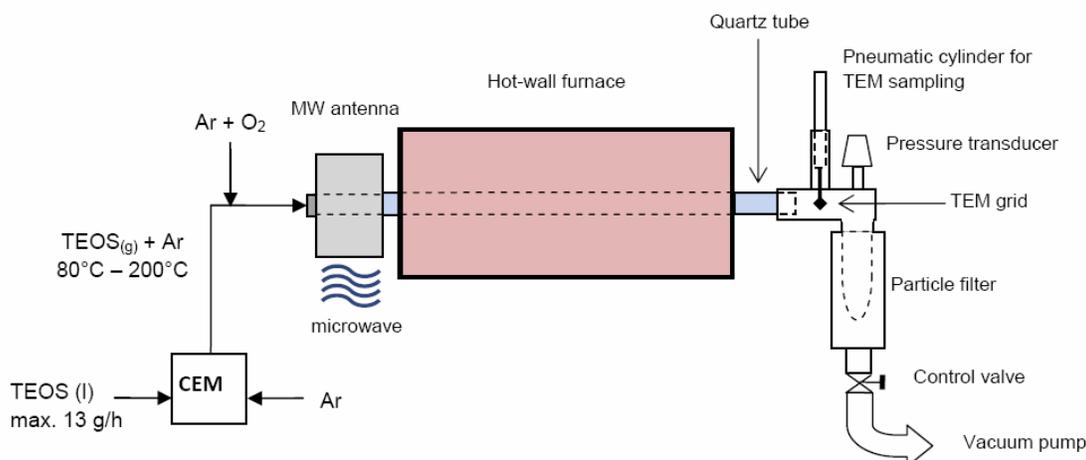


Fig. 1. Schematic of the hybrid microwave-plasma hot-wall reactor.

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 2 and 100 kPa using a control valve and the reactor pressure is varied in order to achieve different residence times. Based on the ideal gas law, the residence time is proportional to the pressure for constant gas flow rate and temperature. 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.

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 utilized supplies gas mixtures that can contain up to 13 g/h of TEOS vapour despite the poor vapour pressure of TEOS (0.22 kPa at 20°C). The tube that connects the CEM and the reactor inlet is heated to 360 K 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 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 collected 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, ex-situ TEM samples were collected from the filter. Furthermore, ex-situ analysis was also carried

out by means of the isothermal Brunauer-Emmett-Teller (BET) nitrogen adsorption method. The primary average BET particle diameter was calculated based on the measured surface area assuming monodisperse 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 ρ is the bulk density of silica (2200 kg/m³), SSA is the specific surface area in m²/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. First, the influence of the TEOS concentration on the particle size was investigated by varying the TEOS flow rate from 1 to 13 g/h (equivalent to 0.3 to 4.0% by mass) while keeping the flow rate of Argon and Oxygen constant at 2.1 l/min and 1.0 l/min, respectively. For these tests, the plasma reactor was used without the hot-wall furnace in order to observe the direct influence of the TEOS concentration on the resulting particle size. 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.

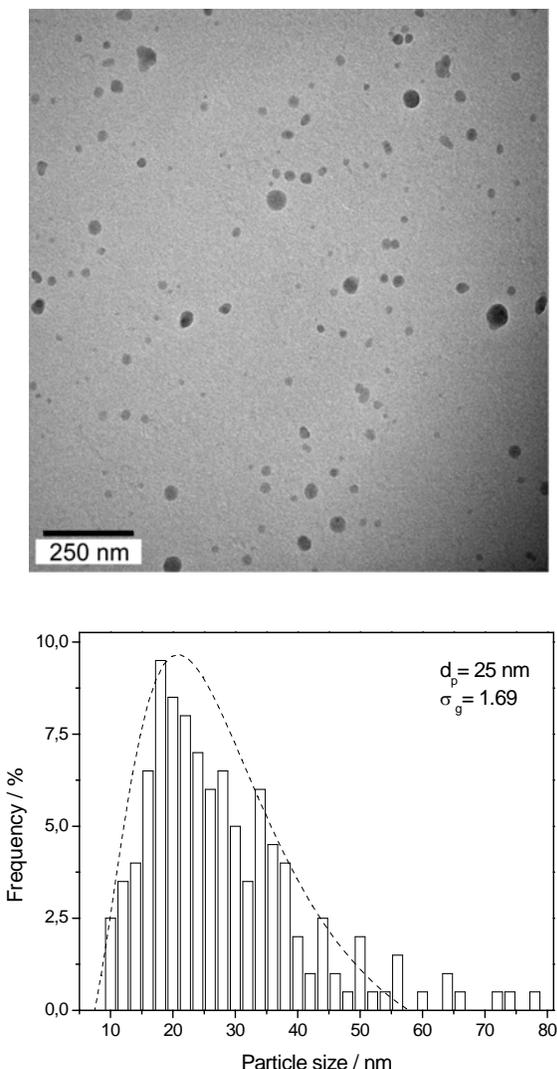


Fig. 2. TEM-image of silica nanoparticles sampled from the reactor chamber. TEOS concentration is 3.0% by mass, reactor pressure is 4 kPa (top); histogram and fitted log-normal size distribution with the mean particle diameter $d_p = 25$ nm and the geometric standard deviation $\sigma = 1.69$ (bottom).

By default, the diameter of about 200 silica nanoparticles observed on the different TEM grids was measured and used to generate a histogram as can be seen from the graph in Fig. 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.

Fig. 3 shows the dependence of the mean particle diameter on the TEOS concentration. Up to TEOS concentrations of 2.2% by mass the particle size increases as expected from 12 nm (0.3% TEOS) to about 28 nm (2.2% TEOS). This is due to the presence of a higher

concentration of silica species with increasing TEOS flow rates, increasing the probability of collision of primary particles. This results in enhanced coagulation leading to larger particles. Fig. 3 also shows that at TEOS concentrations above 2.2% by mass, the particle size slightly decreases. A likely explanation for this could be that at higher TEOS concentrations the nucleation rate is increased, thus, resulting in a higher concentration of primary particles with slightly smaller size. This behaviour is well known and described as collision-limited growth of particles [9].

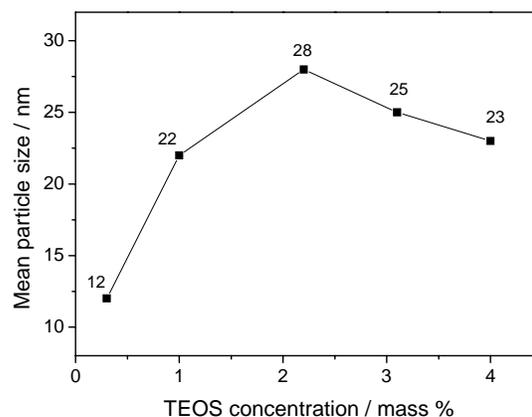


Fig. 3. Influence of TEOS concentration on the mean particle size. Reactor pressure is 4 kPa.

Further tests were carried out by introducing the hot-wall furnace to the reactor setup in order to observe the influence of reduced cooling rates on the particle size. The TEOS concentration was fixed to 1.0% and the furnace temperature was varied from 200°C to 800°C. As observed above, in all cases almost spherical, non-agglomerated particles were found on the TEM grids. Figure 4 shows that up to furnace temperature of 400°C the mean particle size increases as expected, the maximum particle size achieved is 28 nm. However, the particle sizes decrease when the furnace temperature is increased above 400°C. We attribute this to two reasons: As it is expected from plasma synthesis of nanoparticles, Coulomb repulsion seems to play 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 [10]. 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.

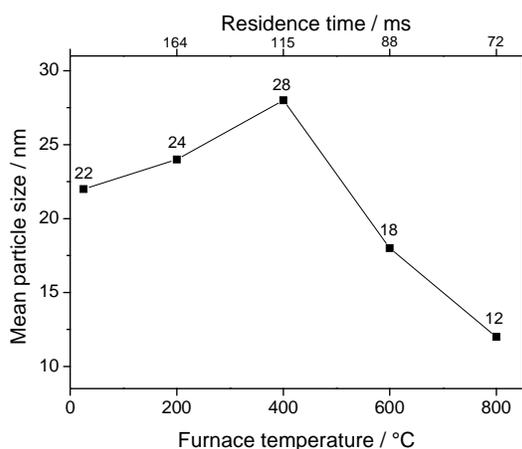


Fig. 4. Influence of the furnace temperature on particle size. Reactor pressure is 4 kPa and TEOS concentration is 1.0% by mass.

To investigate whether the residence time within the reactor influences the particle growth, the TEOS concentration was again fixed to 1.0% and the furnace temperature was adjusted to 800°C while the residence time was increased from 72 to 126 ms by raising the reactor pressure from 4 to 7 kPa. As can be seen from figure 5, the mean particle diameter depends very strongly, and linearly, on the residence time.

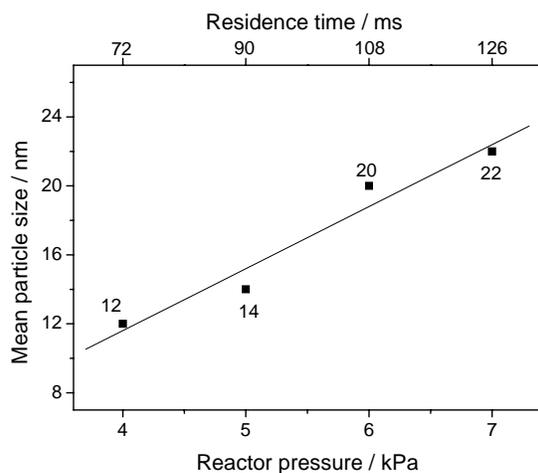


Fig. 5. Variation of the mean particle size with the reactor pressure, and hence residence time. Furnace temperature is 800°C, TEOS concentration is 1.0% by mass, O_2 and Ar flow rates are 1.0 l/min and 2.1 l/min respectively.

From these results it is obvious that we are able to adjust the size of silica nanoparticles prepared by gas-phase synthesis by two independent parameters, namely the TEOS precursor concentration, and the residence time in the hot zone of the reactor.

Nevertheless, 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 (cf. figure 6a). The findings demonstrate that the individual particles in the gas phase are well separated (as it was shown earlier in figure 2) while hard agglomerates are found in the samples taken from the filter. The highest agglomeration index was obtained with TEOS concentration of 2.2% by mass, reactor pressure of 4 kPa 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 (cf. Figure 6b).

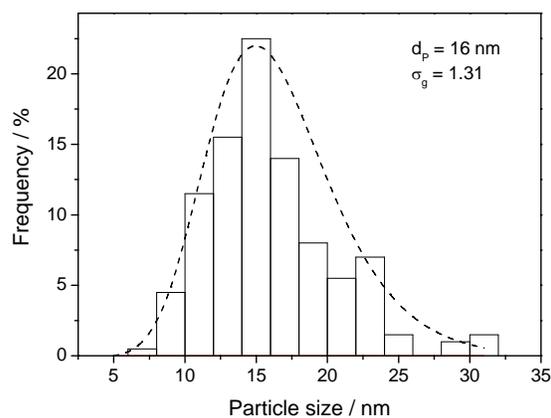
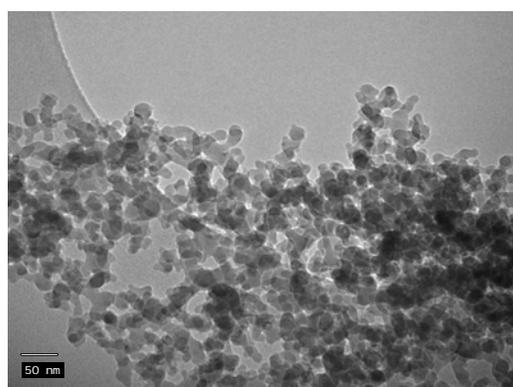


Fig. 6. TEM-image of the collected particles from the filter (top), particle size distribution at TEOS concentration of 2.2% by mass and furnace temperature of 1000 °C (bottom).

The BET particle size of the samples from the filter as shown in figure 6 was 24 nm which is much bigger than that from the material from the reactor. The high agglomeration reduces the specific surface area (SSA) and therefore shows higher particle size. An explanation for 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 [11]. 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 [12]. As a result, we propose that silica nanoparticles that touch each other will sinter together in humid atmosphere due to silanol and silicic acid 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 TEOS concentration, residence time and hot-wall furnace temperature was investigated. The results show that the particle size depends on the TEOS concentration and the residence time in the reactor. Low TEOS concentrations and residence times yield small particles whereas their size increases at higher values. The analysis of the particles from the filter in contrast shows large hard agglomerates. When varying the furnace temperature between 200°C 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.

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References

- [1] A. Gutsch, H. Mühlenweg, M. Krämer, *Small* **1**, 30 (2005).
- [2] S. Tsantilis, S. E. Pratsinis, *J. Aerosol Sci.* **35**, 405 (2004).
- [3] A. Abdali, M. Fikri, H. Wiggers, C. Schulz, 26th Intern. Symp. Shock Waves, **1**, 781 (2009).
- [4] J. Herzler, J.A. Manion, W. Tsang, *J. Phys. Chem. A* **101**, 5500 (1997).
- [5] H. D. Jang, *Aerosol Sci. Technol.* **30**, 477 (1999).
- [6] K. H. Ahn, C. H. Jung, M. Choi, J. S. Lee, *J. Nanopart. Res.* **3**, 161 (2001).
- [7] B. M. Goortani, N. Mendoza, P. Proulx, *Int. J. Chem. Reactor Eng.* **4**, 1 (2006).
- [8] S. Tsantilis, S.E. Pratsinis, *Langmuir* **20**, 5933 (2004).
- [9] T.T. Kodas, M. Hampden-Smith, *Aerosol Processing of Materials*, Wiley-VCH, New-York (1999).
- [10] S. Vemury, S. E. Pratsinis, *Appl. Phys. Lett.* **66**, 3275 (1995).
- [11] J.A.S. Cleaver, J.W.G. Tyrrell, *KONA Powder and Particle* **22**, 9 (2004).
- [12] M.S. Kaliszewski, A.H. Heuer, *J. Am. Ceram. Soc.* **73**, 1504 (1990).

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