

Iron-oxide nanoparticle synthesis from liquid spray flames under variable pressure conditions

S. Hardt^{1,*}, H. Grimm¹, I. Wlokas¹, H. Wiggers^{1,2}, A. Kempf^{1,2} and C. Schulz^{1,2}

¹Institute for Combustion and Gasdynamics, University of Duisburg-Essen

²CENIDE, Center for Nanointegration Duisburg-Essen

47048 Duisburg, Germany

sebastian.hardt@uni-due.de

ABSTRACT

Iron oxide nanoparticles have been synthesized by liquid flame spray pyrolysis of an alcoholic solution of iron nitrate. In this document we focus on the properties of the synthesized iron oxide as a function of synthesis pressure and volume flow of the precursor solution. Six different samples were produced and investigated ex-situ by Transmission Electron Microscopy (TEM), nitrogen adsorption (BET) and x-ray diffraction (XRD). The investigation of the synthesis process was additionally supplemented by a computational fluid dynamics (CFD) simulation of the spray flame and population balance modeling of the particle formation and growth dynamics. Because of their nanometer size and high surface area, these materials are highly interesting for the removal of toxic, sulfur-containing compounds (gas purification) as well as for applications based on non-toxic, magnetic materials, eg. hyperthermia cancer treatment.

Keywords: Iron oxide, nanoparticle synthesis, flame spray pyrolysis, gas-phase synthesis, CFD, population balance equation

1 MATERIALS AND METHODS

Experiments were carried out in an enclosed flame spray pyrolysis system. This enables not only full control of gas flows in the reactor but also absolute pressure control during the synthesis. Figure 1 shows the schematics of the experiment. The solution is supplied via a capillary with an inner diameter of 0.4 mm and an outer diameter of 0.7 mm which is placed in the center of a burner nozzle. An annular gap with an outer diameter of 1.2 mm surrounds directly the capillary. The precursor solution is injected with a variable, pulsation-free volume flow into the reactor by a system of two alternating syringe pumps. A dispersion gas flow (oxygen, Air Liquide, purity 99.95%) from the annular gap atomizes the liquid. It forms a free stream with high exit velocity when entering the reactor which atomizes the liquid and forms a spray. The spray is ignited and stabilized by a surrounding premixed methane/oxygen pilot flame fed from an annular gap with an inner diameter of 10 mm and an outer diameter of 10.4 mm and nanoparticles are formed from precursors dissolved in the liquid fuel. An additional sheath gas flowing through a sintered bronze stabilizes the gas flow in the reaction chamber.

To enable operation at 250 – 1000 mbar absolute pressure, the burner is assembled in a pressure-controlled stainless steel housing. A baghouse filter was used to separate the particles from the exhaust gases and a rotary vane pump on the clean gas side of the filter system ensures the desired pressure within the reaction chamber.

For the synthesis of Fe₂O₃ a solution of iron nitrate nonahydrate (Fe(NO₃)₃ (synthesis grade; Merck) in ethanol (p.a; sigma Aldrich) with a molarity of 0.5 mol/l is used. With respect to the purity of the nanoparticle product it is essential to use a solvent with high purity to avoid contamination or even doping.

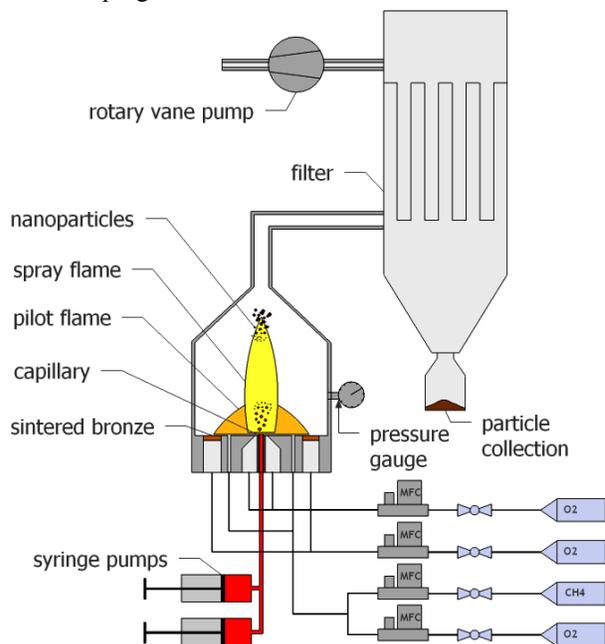


Figure 1 Sketch of the experiment. The pilot flame is a premixed methane/oxygen flame burning around the capillary and the dispersion gas inlet. Four calibrated mass flow controllers control the sheath gas, the dispersion gas and the pilot flame supporting gases.

Experiments were done at varying pressure of $p_1 = 250$, $p_2 = 500$ and $p_3 = 1000$ mbar. The flow rate of dispersion gas was set to 7000 sccm (standard cm³/minute), the flow rate of the pilot flame was 1500 sccm CH₄ and 4000 sccm O₂ and the sheath gas flow rate was 4000 sccm O₂. Two series of experiments were carried out with a volume flow of the precursor solution of 5 ml/min and 7 ml/min, resp.

Numerical simulation

The numerical simulation was carried out in two major steps: (a) A three-dimensional reacting flow simulation of an ethanol spray flame and (b) a subsequent simulation of the particle population balance along the central stream line. The simulation of the particle synthesis process is in an early stage and only indirectly validated through ex-situ measurements of mean particle diameters.

For the simulation of the spray flame we used the computational fluid dynamics software OpenFOAM. In scope of our model, the blast atomizer nozzle was simplified into a circular pipe with the dispersion gas and a disc injector for the liquid. The initial distribution of the spray cloud was modeled using the Rosin-Rammler model; the outer spray angle was set to 10°. Our model is highly empirical, as it does not contain the initial spray formation and break-up of the liquid. Further, the dispersion gas velocity was set artificially to a low value – in reality the dispersion gas is flowing at critical velocity. Despite the rough simplifications in the description of the atomization process, we could reproduce the velocity and temperature distribution of the spray flame with plausible values.

The equations for the particle dynamics are solved along the central streamline with the transport velocity and temperature extracted from the three-dimensional CFD simulation. A monodisperse model was used for the population balance equations to simulate the particle formation and growth, which is basically a method of moments with a prescribed particle-size distribution function [1]. Here, the considered moments are the monomer concentration n_1 , the local particle number density N_∞ and the particle surface area A_∞ . The transport of the moments along a streamline s is described by the equations:

$$\frac{d}{ds} \left(u_s n_1 - D_1 \frac{d}{ds} n_1 \right) = -J$$

$$\frac{d}{ds} \left(u_s N_\infty - D_p \frac{d}{ds} N_\infty \right) = J - \frac{1}{2} \beta N_\infty^2$$

$$\frac{d}{ds} \left(u_s A_\infty - D_p \frac{d}{ds} A_\infty \right) = J a_1 - \frac{A - A_{\min}}{\tau_c}$$

where u_s is the transport velocity at the streamline, D_1 and D_p are the diffusion coefficients, and β is the coagulation coefficient for the free-molecular regime. The monomer concentration n_1 is calculated directly from the rate of formation J of the particle species Fe_2O_3 and a_1 is the monomer surface area. The rate of formation of iron oxide particles is assumed to be equal to the reaction rate of ethanol combustion. The characteristic coalescence time τ_c can be described by:

$$\tau_c = A_C T \cdot d_{pp}^4 \exp\left(-\frac{T_a}{T}\right)$$

The parameters for $A_C = 8 \times 10^{16} \text{ s}/(\text{K m}^4)$ and $T_a = 30,000 \text{ K}$ were received from a fitting procedure to data provided by Janzen et al. [2, 3].

2 RESULTS

Experimental results

The synthesized particles were characterized ex-situ via XRD (PANalytical X-Ray Diffractometer X'Pert PRO with Cu-K α radiation) to investigate particle composition and crystal size (calculated by Rietveld refinement using the program MAUD), BET measurements (Quantachrome Nova2000) to measure the specific surface area and to calculate the particle diameter assuming monodisperse, spherical NPs, and TEM to visualize morphology, size and agglomeration.

From the XRD-analysis it is obvious that pure $\gamma\text{-Fe}_2\text{O}_3$ is produced in all six cases. The XRD pattern of particles synthesized at a precursor volume flow of 7 ml/min and a synthesis pressure of 1000 mbar and 500 mbar show the highest peak intensities and from Rietveld refinement we received a crystallite size of 17 nm. The smallest particles with a size of 8 nm were observed for a volume flow of 5 ml/min and a system pressure of 250 mbar.

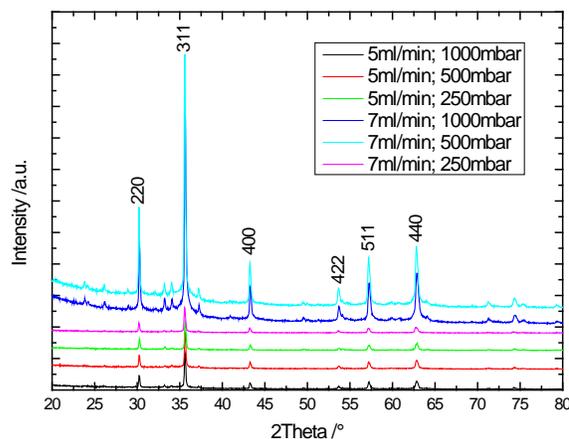


Figure 2 X-ray diffraction measurements for all six samples; It is obvious that the precursor volume flow has an influence on the particles size. The influence of the pressure during synthesis becomes more important at values below 500 mbar.

The specific surface area (SSA) measured by five point nitrogen adsorption using the Brunauer, Emmet, Teller-method (BET) was found to be in the range of 70 to 120 m²/g. Assuming monodisperse, spherical particles and the bulk density of $\gamma\text{-Fe}_2\text{O}_3$, the mean particle size d_p can be calculated from

$$d_p = \frac{6000}{\text{SSA} \cdot \rho_p}$$

As a result, mean particle diameter between 10 and 18 nm were found which is in good agreement with the values received from X-ray diffraction. Nevertheless, some aggregation can be assumed. Therefore, the morphology and the state of agglomeration were investigated by transmission electron microscopy (TEM) using a Philips CM12 with an accelerating voltage of 120 kV. For the preparation of the TEM specimens the nanoparticles were dispersed in ethanol (p.a.; Merck) through sonication and

TEM-grids were prepared by dip-coating. Typical results received from particles synthesized at 250 mbar is shown in figure 3. The synthesized particles have a mean diameter of 10 ± 3 nm and are partly sintered resulting in aggregates with a typical size between 30 and 370 nm. In summary it is found that the particle sizes measured by XRD as well as by BET increases with pressure and with the precursor volume flow (precursor concentration). It was also found that the influence of pressure on the particle size is not as large as the influence of the precursor/dispersion gas flow rates.

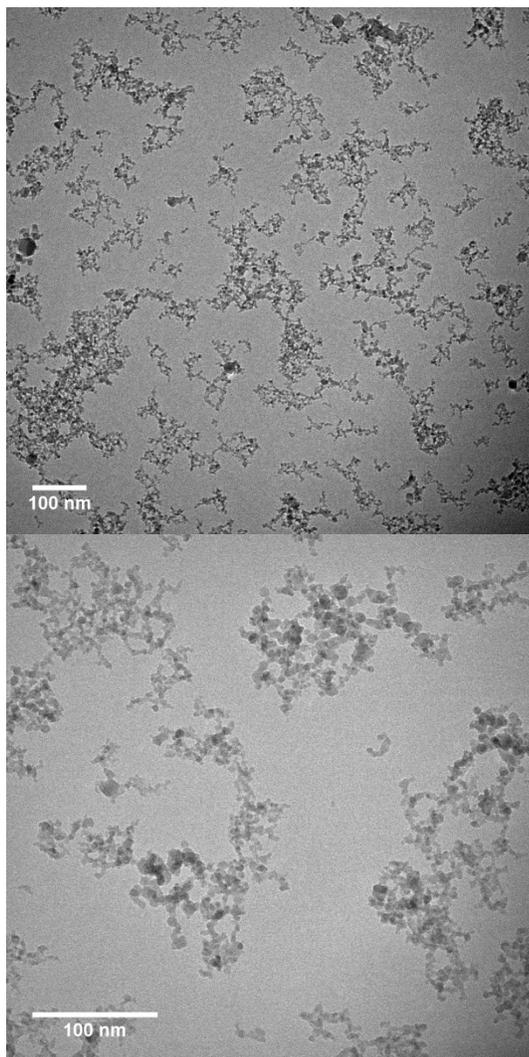


Figure 3 A typical low-magnification TEM image of the as-prepared particles (upper) and a more detailed view of agglomerates (lower image). Scale bars: 100 nm.

A higher TEM resolution shown in figure 4 indicates that the particles are mostly softly-agglomerated and have a roundish shape. The energy-dispersive X-ray spectroscopy (EDX) shown in figure 4 confirms that the particles produced in the reactor only consist of iron and oxygen, the signals observed for copper and carbon originate from the supporting TEM grid.

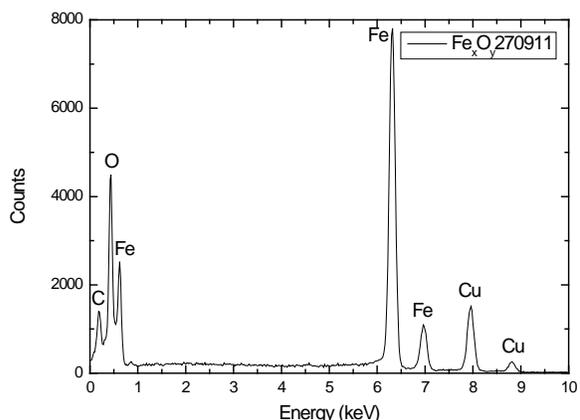
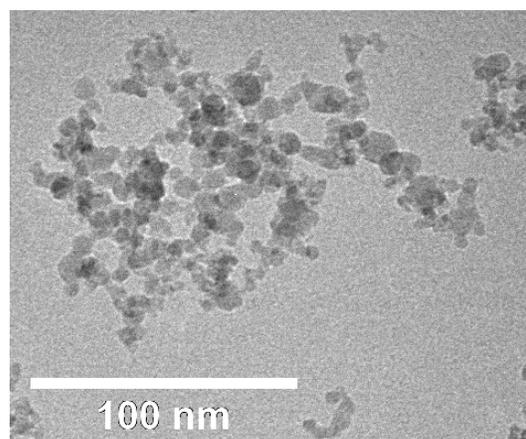
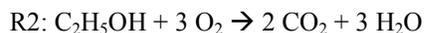
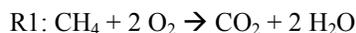


Figure 4 (upper image): A detailed TEM image of an agglomerate consisting of iron oxide nanoparticles; Scale bar: 100 nm. Lower image: EDX spectrum of a region from the TEM grid (right).

Numerical results

The first step in the numerical simulation was the calculation of the flow field, i.e., velocity, temperature and turbulent reaction rates in the reactor. The CH_4/O_2 combustion in the pilot flame and the combustion of the ethanol vapor were described with global reactions



The major drawback of this description is, that the precursor-flame interaction cannot be described properly. It is well known, that the presence of iron species has a large impact on the flame chemistry, which can be only modeled properly with a detailed finite rate kinetics mechanism. Nevertheless, we rely on the result calculated with the global reaction mentioned above, as the transport velocity, the local iron oxide monomer density and the temperature history are the most influential parameter for the particle growth downstream the flame and not the flame chemistry itself.

Quantity	Value
Operating pressure	1 bar
Liquid mass flux	2.6×10^{-5} kg/s
Dispersion gas flux	7000 sccm O ₂
Pilot flame	3000 sccm O ₂ , 1150 sccm CH ₄
Sheeth gas	5000 sccm O ₂
Inert gas flux	3×10^5 sccm N ₂

Table 1 Operating conditions used for the simulation. The liquid was a 0.5 mol/l solution of Fe(NO₃)₃ in ethanol. The inert gas was fed into the reactor for window flushing and diluting the exhaust gas to prevent condensation of water.

The operating conditions used to simulate the reactor are listed in Table 1. As the spray model requires a three-dimensional representation of the geometry, the reactor geometry was represented as a symmetric 30° section with cyclic boundaries. The angle of the section was chosen according to mesh cell quality requirements.

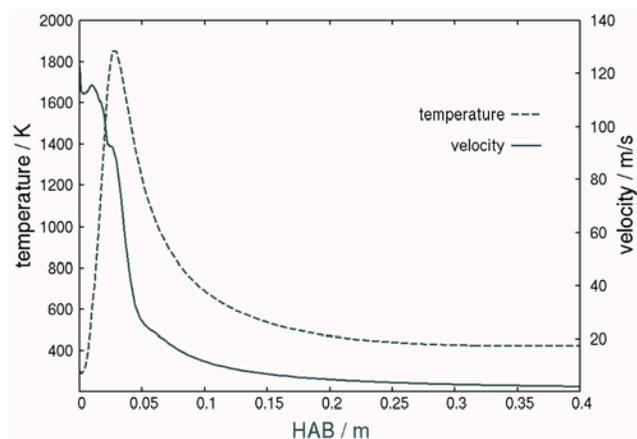


Figure 5 Temperature and the transport velocity at the central streamline plotted for the height above burner (HAB). The initial velocity of the dispersion gas was $u = 122$ m/s.

The result of the complex spray flame simulation is required as input for the one-dimensional population balance model. Figure 5 shows the computed temperature and the transport velocity at the axial streamline. Due to the very high velocity of the spray jet, the temperature gradient is quite steep. Because of the short residence time in the hot region, the main formation of particles takes place downstream the flame. The mean particle diameter and the iron oxide particle formation and growth are shown in Figure 6. A value of $d_p = 8$ nm 0.4 m downstream the nozzle (HAB = height above burner) is in very good agreement with the experimental results as the measured particle diameter of material sampled from the filter is almost identical. As a result it can be stated that our simplified model is able to describe the spray-flame assisted synthesis of nanoparticles. It is obvious that the particle growth is mainly determined by the coagulation in the “post-flame” regime. Thus, the assumption that the flame chemistry itself has a negligible influence on the particle formation seems to be reasonable.

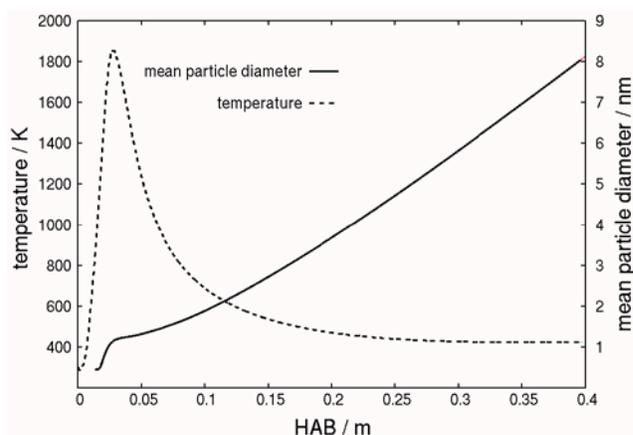


Figure 6 Temperature and the mean particle diameter as function of HAB. While the first particles are formed in the spray flame, the later growth (after HAB = 0.1 m) is dominated by coagulation.

3 CONCLUSIONS

The influence of synthesis pressure and volume flow rate of precursor solution on particle size and crystallinity of iron oxide nanoparticles was investigated. Iron oxide particles were synthesized via flame spray pyrolysis under variation of operating pressure, precursor volume flow and dispersion gas flow rate. In contrast to atmospheric systems the spray pyrolysis reactor presented here is able to operate at pressures as low as 250 mbar. Iron oxide nanoparticles with mean particle diameter between 8 and 18 nm could be synthesized depending on pressure and precursor concentration. It increases with pressure and with the precursor volume flow. It was found that the influence of pressure on the size is not as large as the influence of the precursor/dispersion gas flow rates. No influence of pressure on the crystal phase was found. With this reactor system production rates of 10–20 g/h were reached. Recent experiments showed that the influence of pressure on the mean particle size can be increased by increasing the residence time of precursor in the hot region of the reactor so by decreasing the velocity of the spray.

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