Synthesis of Nanosized Oxidic Particles by Ultrasonic Spray Pyrolysis

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Abstract. Synthesis of nanosized spherical aluminium oxide (Al_2O_3) particles from inorganic metallic-salt precursor was achieved by ultrasonic spray pyrolysis method. The size distribution and morphology of prepared oxidic particles are characterized by SEM. Precursor system was tested in order to investigate proposed mechanism for synthesis. The optimum experimental conditions for the various oxidic particle synthesis have been proposed. The prepared naoparticles are going be used for improving mechanical properties of gold layers in electrical contacts, without decreasing electrical conductivity of these contacts.

Introduction

Aluminium oxide (Al_2O_3) is today a highly-valued material because it can be applied in many fields of engineering, such as coatings, heat-resistant materials, abrasive grains, cutting materials and advanced ceramics. Possibility for such a broad field of application of aluminium oxide lies in its excellent properties such as chemical inertness, high resistivity, high hardness, high abrasive and corrosive resistance and high thermal conductivity [1-2]. Aluminium oxide is most commonly produced in the form of powders, but it can be also obtained in a form of dense coatings, thin films or bulk solids. There are several different methods to synthesize nanoparticles. Most common methods for aluminium oxide production are different liquid phase methods which include sol-gel processing, solution combustion decomposition and vapour deposition, and vapour/aerosol phase methods like spray pyrolysis and laser pyrolysis. Sol-gel techniques provide very good control of particle size and morphology, narrow particle size distribution, but they are consisting of complex systems which are including expensive organic solvents, so that later recovery of solvent is necessary and they are not suitable for scale-up. Vapour/aerosol phase methods offer certain advantages over the liquid phase methods, as they are simple, rapid and continuous and they provide good control of particle size and particle size distribution by controlling different process parameters [3]. The ultrasonic spray pyrolysis is very convenient method for synthesis of nanoparticles that provides good control of particle size and narrow particle size distribution and it is suitable for usage of available and cheep precursors [4-5].

According to previous studies [6], in a lab-scale ultrasonic spray pyrolysis, aluminium oxide was produced from inorganic aluminium salts by ultrasonic spray pyrolysis. In this work aluminium oxide (Al_2O_3) nanoparticle were prepared by ultrasonic spary pyrolysis (USP) and the generation of Al_2O_3 nanoparticles in USP was investigated by manipulating carrier gas velocity as well as precursor molar concentration as key experimental variables. The main aim of this research was production of spherical Al_2O_3 nanoparticles that are going to be further tested and used for improvement of mechanical properties of gold layers in electrical contacts.

Experimental

Aluminium nitrate $Al(NO_3)_3 \cdot 9H_2O$ and aluminium chloride $AlCl_3 \cdot 6H_2O$ (Merck, Darmstadt, Germany) were used as precursor for the synthesis of aluminium oxide nano powder by ultrasonic spray pyrolysis. The solutions were prepared by dissolution of equivalent of amounts of corresponding salts in deionised water. Equipment used for experiments is described in previous work of (S.Stopic et al.)[7]. The equipment consists from the ultrasonic atomizer, the reactor with three separated heating zones and an electrostatic precipitator. The temperature and pressure control was adjusted by using a thermostat and a vacuum pump. Atomisation of aluminium salt solution and production of aerosol took place in an ultrasonic atomizer (Gapusol 9001, RBI/France) with three transducers operating at resonant frequency of 2,5MHz. Generated aerosol was carried in the reaction zone with nitrogen gas flow of 3,5-14 l/min. The reaction zone (quartz tube l=1,5m, d=42mm) was heated to temperature of 800°C, with preheating zone and cooling zone at 300°C. For the characterization of the obtained aluminium oxide nano-particle was used scanning electron microscope. SEM images were used for observation of particle size, particle morphology and particle size. Qualitative analyses and estimation of impurity level was performed by energy disperse spectroscopy (EDS) analysis with a Si(Bi) X ray detector, connected with SEM and a multi-channel analyzer. Particle size and particle size distribution were determined by SEM image analyses with ImageJ softer, while experimental data were processed by the computer program Origine8.

Results and discussion

Experimental conditions for the preparation of the aluminium oxide nano-particles are given in Table 1. Experimental parameters were chosen in means of testing influence of different precursors, concentration and gas flow on particle size distribution and morphology.

Test No.	Precursor	Temp. [°C]	Conc. [mol/l]	Gas flow [l/min]
1.	$AlCl_3 \cdot 6H_2O$	800	0,05	3,5
2.	$Al(NO_3)_3 \cdot 9H_2O$	800	0,1	3,5
3.	$Al(NO_3)_3 \cdot 9H_2O$	800	0,05	3,5
4.	$Al(NO_3)_3 \cdot 9H_2O$	800	0,025	3,5
5.	$Al(NO_3)_3 \cdot 9H_2O$	800	0,0125	3,5
6.	$Al(NO_3)_3 \cdot 9H_2O$	800	0,025	7
7.	$Al(NO_3)_3 \cdot 9H_2O$	800	0,025	14

Tabele1: Experimental conditions

The influence of start precursor was tested by using two different aluminium salts $AlCl_3 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$. As shown in Fig. 2a, particles obtained by USP from $AlCl_3 \cdot 6H_2O$ as precursor are irregular sphere shape, with high porosity (nanometar pores) and with partially destroyed particles. In Fig. 2b we can see that particles obtained from $Al(NO_3)_3 \cdot 9H_2O$ as precursor are mostly regular sphere, with smooth surface. Reason for this difference in morphology is different behaviour of precursors during thermal process. $AlCl_3 \cdot 6H_2O$ evaporates from the particle surface leaving craters and causing irregularity in particle shape while $Al(NO_3)_3 \cdot 9H_2O$ melts. Since goal of this research was obtaining spherical Al_2O_3 nano powder, further tests were run only with $Al(NO_3)_3 \cdot 9H_2O$ as precursor.

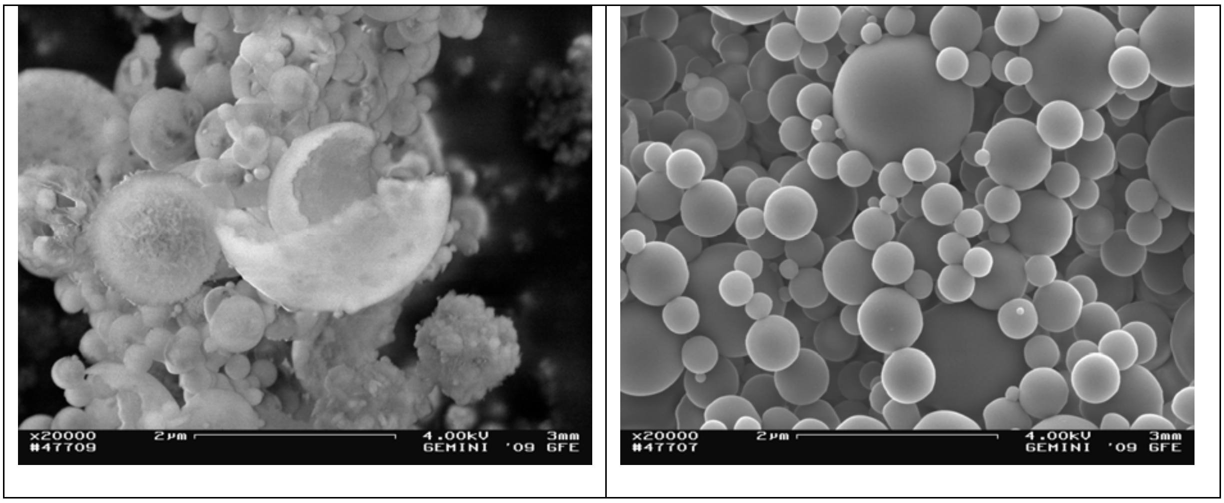


Fig.2: SEM micrographs of Al_2O_3 powders obtained from $AlCl_3 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$

In order to determine influence of concentration of precursor solution and nitrogen flow rate we conducted experiments with variation of these parameters. Results are presented in Fig.4. From SEM image it is clear that in all experimental conditions spherical nano particle were obtained. Influence of precursor solution concentration is in accordance with earlier determined theoretical models where it is expected that particle size decrease with decrease of precursor solution concentration as it is shown at Fig.3a. [8-9]. From experimental results it can be concluded that increase of carrier gas flow rate have positive influence on particle size distribution by decreasing dispersity of particles diameters. This correlation is presented in Fig.3b.

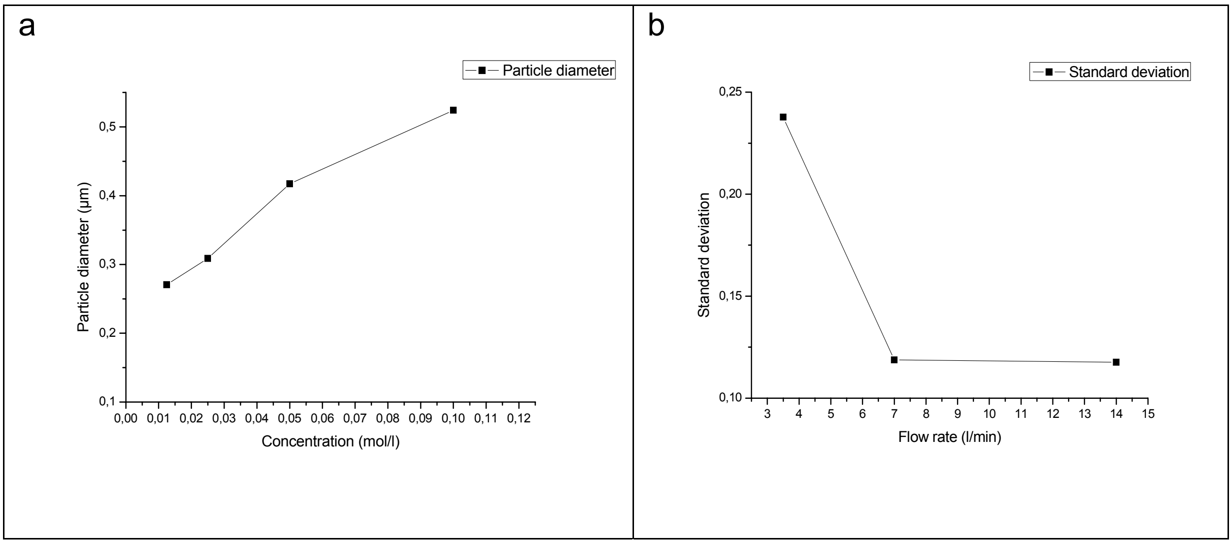
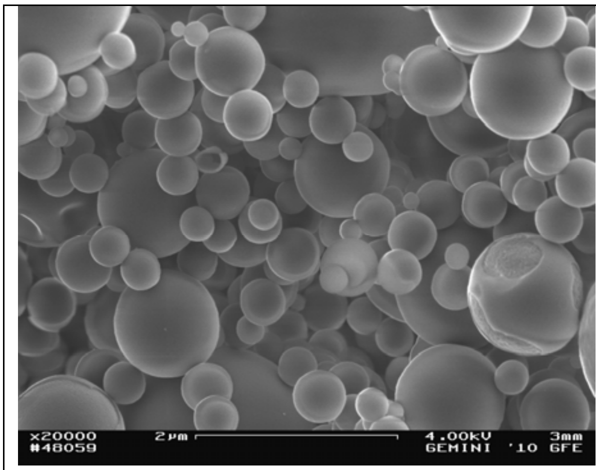
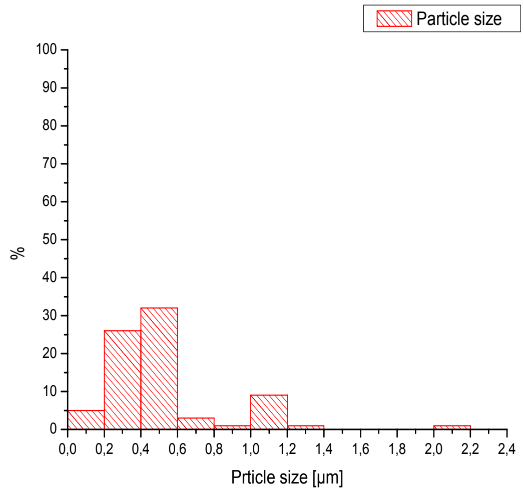
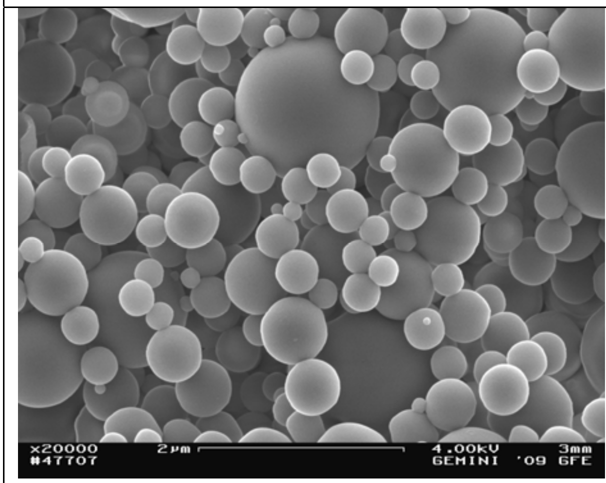


Fig.3: The influence of precursor concentration on particle size (a) and carrier gas flow rate on particle size dispersion (variability) (b)

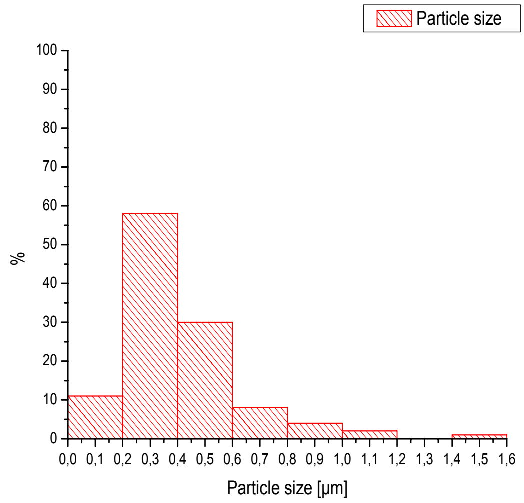


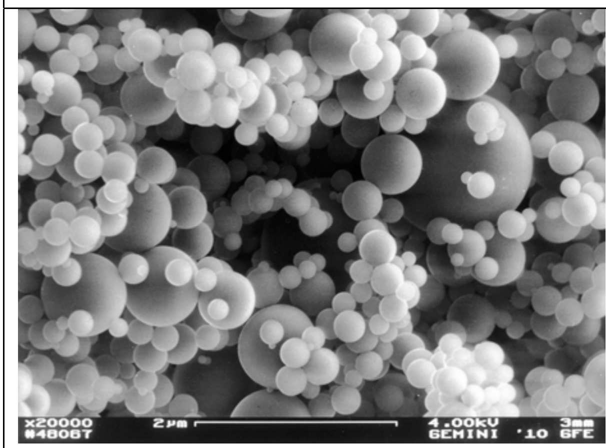
c=0,1 mol/l, q=3,5 l/min



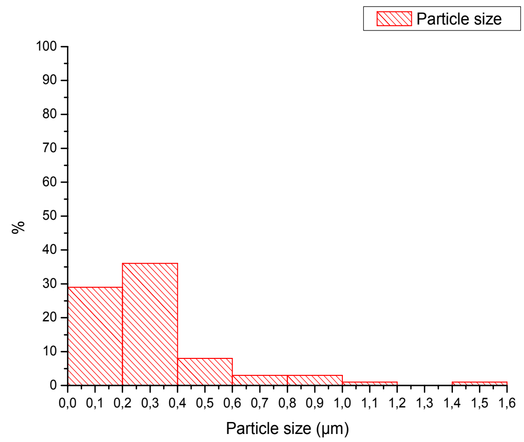


c=0,05 mol/l, q=3,5 l/min





c=0,025 mol/l, q=3,5 l/min



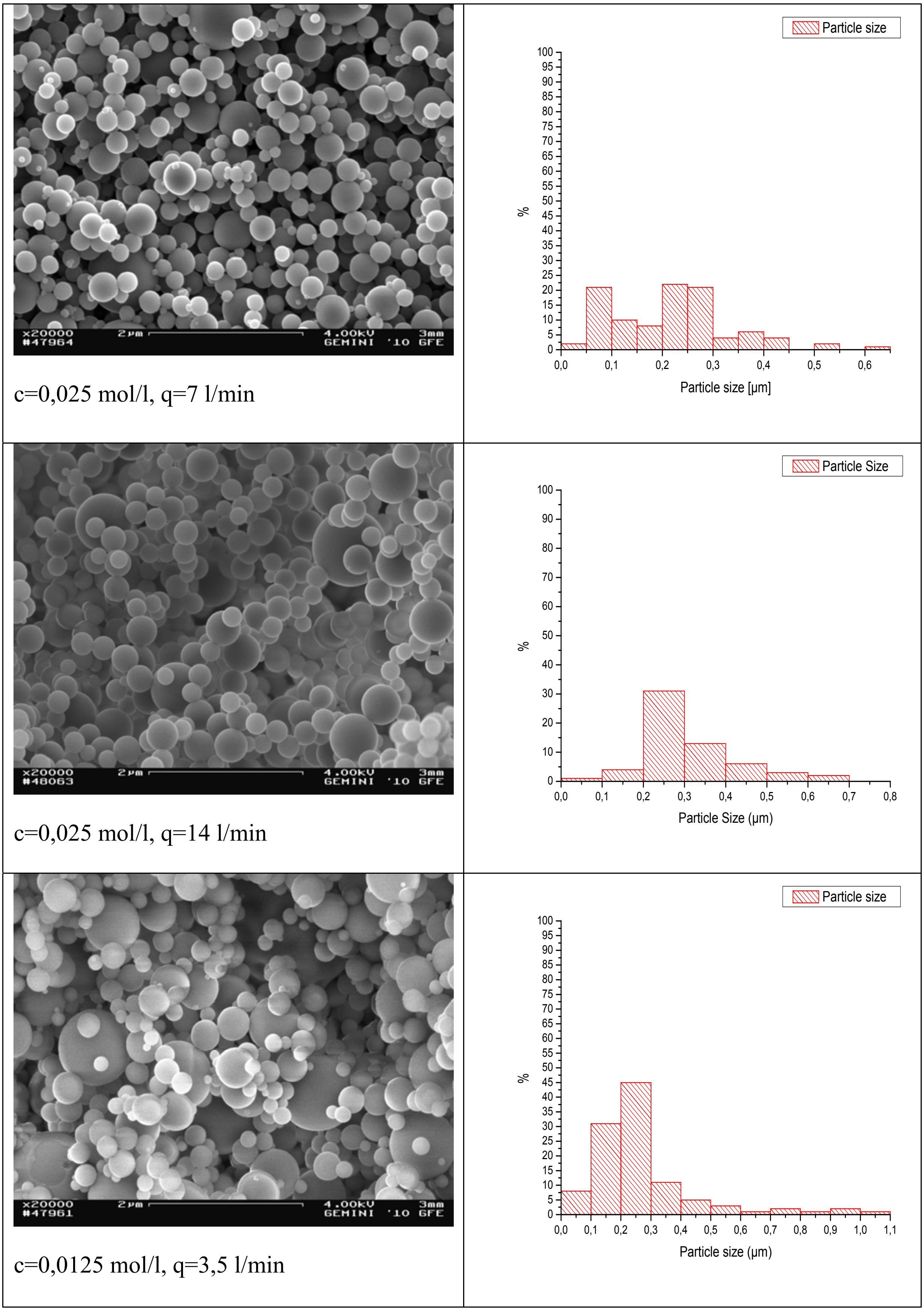


Fig.4: SEM micrographs of Al_2O_3 powders obtained in different experimental conditions and particle size distribution of obtained powders

Qualitative EDS analysis of obtained powder has confirmed that Al_2O_3 was obtained in all experiments. Characteristic result is shown in Fig.5.

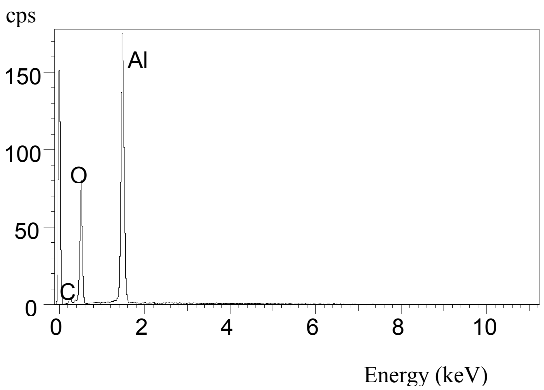


Fig.5: EDS analysis of Al_2O_3 nanoparticles particles

Conclusion

According to experimental results, it is possible to produce Al_2O_3 nano particle by ultrasonic spray pyrolysis. Obtained powder has ideally spherical form if $Al(NO_3)_3 \cdot 9H_2O$ is used as precursor. The best results (small particle size and narrow particle size distribution) were obtained at low precursor concentration and high flow rate of carrier gas. Our assumption is that by increasing flow rate we decrease coagulation rate of aerosol droplets and as a result avoid building of bigger particles that are present in probes with lower flow rate.

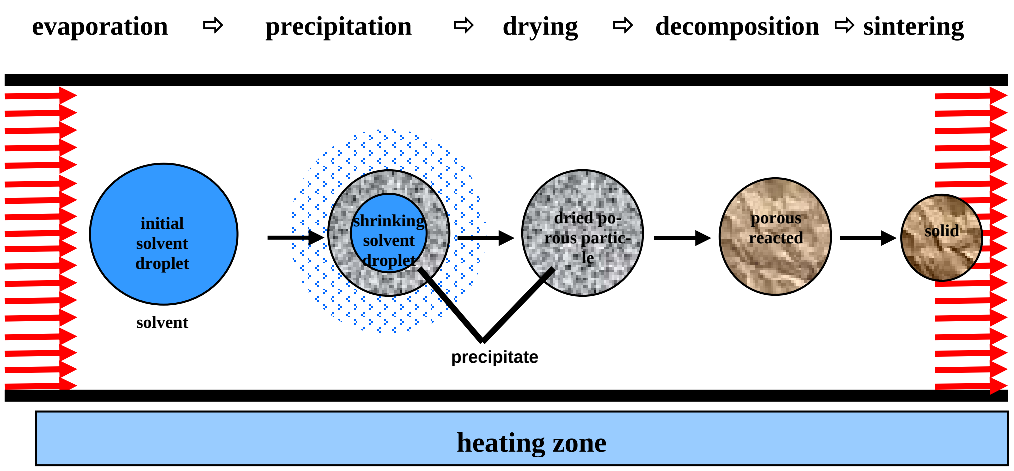


Fig.1: Different steps during a production of nano particle in an ultrasonic atomiser

In previous work model for different steps during a production of nano particle by an ultrasonic spray pyrolysis is given, as presented in Fig.1. [10]. In the further work theoretical model of influence of precursor concentration and carrier gas flow rate on particle size is going to be developed.

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