1 Introduction

1.1 Motivation

Particle granulation and coating processes are today ones of the major developments of fluidized bed technology in industrial fields such as the chemical, pharmaceutical, cosmetic and food industries [Salman *et al.* [2007], da Silva *et al.* [2014]]. The processing in fluidized bed systems significantly improves the properties of final products, e.g. by providing barrier properties for heat, moisture, oxygen or light, improving mechanical properties, creating a prolonged release of active ingredients, reducing dust formation, extending shelf life or broaden the fields of application. Moreover, the proper variation of process conditions enables tailoring the material properties into the desired state and adjustment of particle size, shape or density [Salman *et al.* [2007], da Silva *et al.* [2014]].

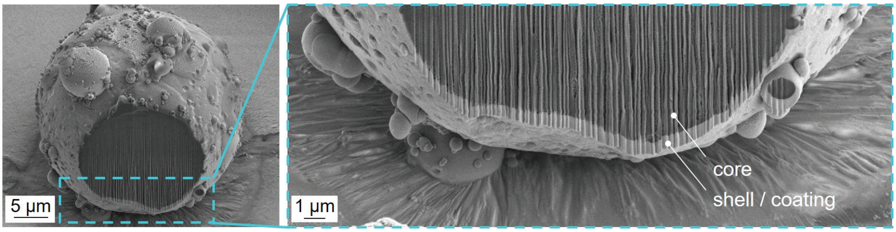

Fig. 1.1: Cross-sectioned aerogel particle with visible core and coating layer.

During a coating process the surface of solid particles is covered with a thin layer of a solution, a suspension or a melt, which is atomized onto the bed in a fluidized state. The small droplets of the coating agent are wetting the solid, spreading on its surface and drying or solidifying depending on the used material, creating a crust [Kumpugdee-Vollrath *et al.* [2011]], as shown in a cross-sectioned aerogel particle in Fig. 1.1, which was spray coated in a spouted bed. Thus, depending on the coating material type and process conditions, film or hot melt coating are performed. The layer growth is related to a certain residence time of the particles in the spray zone and the fluidization conditions resulting in intensive mixing and heat and mass transfer. The expected layer thickness is significantly lower compared to layers applied in a granulation process. The aggregation of single particles into agglomerates is not desired and only individual particles coated homogeneously with a thin layer are expected. Thus, the film or hot melt coating processes are very challenging and require careful and precise controlling of process conditions, like fluidization air flow rate, bed temperature, nozzle air pressure or spray rate of the coating agent, in order to design a core-shell structured particle at high process stability. Thus, the process is very complex and capturing of single influences caused by the variation of the process conditions is not possible. At once a uniform application of the coating layer is required and agglomeration, bed collapse or particle elutration are avoided. Additionally, the handling of irregularly shaped, very fine and light or very large particles is improved by processing in spouted beds. In spouted beds the gas is introduced into the system by inlet slits instead by a gas distribution plate and a high velocity spout or jet in the middle of the apparatus is formed causing a structured particle movement in the bed. Thus, particles which are difficult to handle in common fluidized beds due to their size or shape, can still be fluidized and processed. At the same time due to characteristic particle movement the coating process chain consisting of spraying, spreading and drying takes place in one cycle. Ideally, the particles entering a new cycle are dry and thus, could be coated again without creating agglomerates.

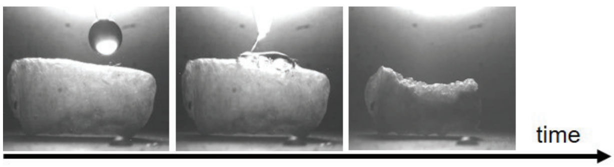

Fig. 1.2: Influence of water droplet exposed on aerogel monolith on its structure with time.

The bed stability during fluidization is a key factor influencing the result of the coating procedure [Parise *et al.* [2011]]. Is the stable fluidization interrupted once, the success of the current batch may be threatened. The defluidization is characterized by the appearance of zones with no activity causes agglomeration of single particles and local reduction of heat and mass transfer coefficients. It appears mostly due to a too high moisture content of the bed and causes aggregation of the particles. The local defluidization can lead fast to the collapse of the entire bed. Thus, moisture content, spray rate, fluidization air flow rate or particle type play an important role for the bed stability and have to be monitored [Stergar *et al.* [2016]].

The spouted bed coating improves or modifies properties of primary particles and thus, opens new application fields. A very interesting group of materials according their properties and potential application is represented by aerogels. Principally, aerogels are characterized by very high porosity (up to $99\,\%$) and open pore structure, resulting in many beneficial properties, as low thermal conductivity or high adsorptive potential. Depending on the type of used precursor (inorganic, organic or hybrid) and the preparation method the characteristics and shape of resulting aerogel differ. Therefore, the potential of the aerogels has not been fully exploited yet. Especially, the organic aerogels attracted much interest in various biomedical or food applications. Organic material, such as polysaccharides, are derived from renewable resources, are cheap and easy to process, biocompatible and often biodegradable. The combination of the above listed factors with the possibility of loading the mesoporous structure with valuable substances and the latitude in selection of the size makes the application of such products almost unlimited. Nevertheless, the structure of aerogels is often very fragile and sensitive to the storage conditions. When exposed to humid conditions or contacted with liquids, the porous network of aerogels collapses irreversibly, as shown in Fig. 1.2.

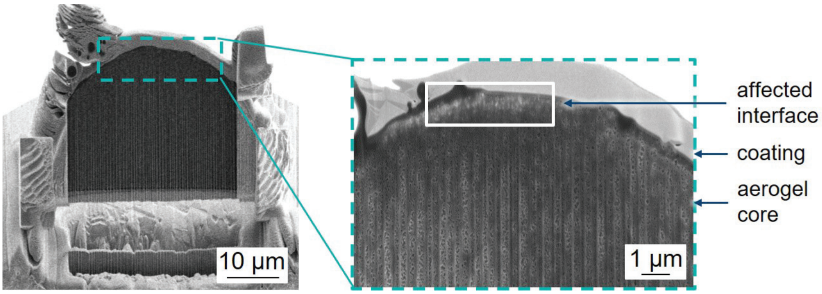

Fig. 1.3: Lamella prepared with focused ion beam from a coated aerogel particle for investigation of the coating quality with transmission electron microscope (TEM): lamella before thinning (right) and prepared lamella investigated with TEM plug-in (left). The interaction between the coating and the aerogel matrix is marked with a white rectangle. Not published results accompanying Goslinska *et al.* [2019b].

Consequently, further processing and usage of these aerogels is not possible. Thus, both, the aerogels itself as well as the incorporated substance within the pores, can be protected from the influence of environmental factors by a secondary coating layer on the aerogel particle surface. The encapsulation of the aerogels with polymeric coatings is an actually growing and very promising field. Once applied, the coating layer provides many beneficial improvements and additional properties, like enhanced mechanical stability, extended shelf life, protection against moisture or oxygen during storage, taste or odor

masking as well as improved sensory effects, easier product intake or controlled release profile of encapsulated drug.
Nevertheless, the aerogels are very fragile and their three dimensional porous structure may be affected or collapse during coating, as shown in Fig. 1.3. The possible subprocesses occuring during aerogel processing in a fluidized bed are shown schematically in Fig. 1.4.

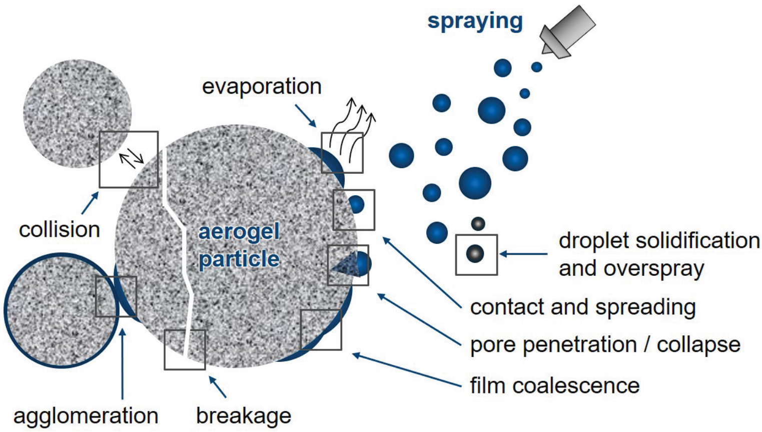

Fig. 1.4: Subprocesses occuring during coating of an aerogel particle.

The appropriate selection of process conditions and apparatus design are then the key elements of the successful encapsulation. The usage of a spouted bed provides good stability while processing small size and low density aerogels. The goal is to design a coating process resulting in structured core-shell particles with unaffected porous structure and uniform coating layer.

1.2 Objectives and scope of the thesis

The central objective of this PhD thesis is to perform experimental investigations on application of thin coating layers on mesoporous particulate systems without changing their initial structure using a spouted bed system. The main goal of the study is to create a barrier between the particle and the environment and enhance its stability during storage as well as extend the range of application, e.g. as pharmaceutical or food matrices. This is achieved by conducting a series of integrated steps listed below:

- study on material properties and giving a recommendation, which kind of materials, melts or solutions, are suitable for coating of mesoporous particles, such as organic aerogels, and which conditions are needed for solidification of the coating agent before it penetrates the pores and changes their structure;

- investigation of the drying behaviour of the solution based coatings and determination of the evaporation rates depending on the process conditions and solid content in order to get practical and physical insights into the evaporation process of single coating droplets and its potential application for lab-scale processes;

- down-scaling of the coating process to the single particle level in order to reduce the influence of simultaneously occurring sub-processes in the spouted bed system, like collision, agglomeration, overspray, breakage or attrition, and the assessment of the influence of process conditions on the particle structure;

- determination of crucial process conditions (temperature, particle size, nozzle air pressure, spray rate, solid amount of the coating or droplet size distribution) influencing the result of the coating process;

- design of a coating procedure for aerogels on multiple particle level in a spouted bed and ensure stable processing without particle agglomeration, bed collapse and lost of coating quality in order to design core-shell particles while keeping their initial structure;

- validation of the results captured using the down-scaled coating method with the multiple particle coating technique and comparison of the influence on the process conditions on the coating quality.

1.3 Outline of the thesis

This thesis is divided into following chapters:

- Chapter 1 - This chapter provides a background to the subject and details the objective and the scope of the thesis. The outline of this work is also presented in this part.

- Chapter 2 - The description of the theoretical background is given in this chapter. First, the spouted bed technology and its application for coating of light and porous particles is introduced. The mechanisms of drying and layer growth are described in detail. The second section is dedicated to the aerogels, their synthesis and application for food and pharmaceutical products. The overview over the state of the art for coating of mesoporous and fragile particles is also given in this chapter.

- Chapter 3 - This part is divided into two main sections. The first section describes the materials used for coating of aerogels. Thus, two different kinds of coating agents, a melt and a solution based coating, are presented. The preparation technique for polysaccharide aerogel beads, which are used as model particles for light weighting and mesoporous materials, is introduced. The second section encompasses the methods for characterization of coatings properties and particle properties as well as the methods used for coating. Thus, the setup for investigation of evaporation rates of coatings is presented. The development of the devices and techniques for coating on single particle level and multiple particle level are described.

- Chapter 4.1 - The properties of the model material particles, synthesized from a polysaccharide and not treated by coating, are studied in this part.

- Chapter 4.2 - This chapter examines the properties of coating agents and their applicability for coating of aerogel beads in spouted bed systems. Thus, the differences between melts and solution based coatings are specified and the recommendation for process conditions during coating are given.

- Chapter 4.3 - This chapter is dedicated to the investigation of drying of single levitating droplets. Thus, the evaporation rate coefficients of solution based coatings are obtained using the acoustic levitator setup.

- Chapter 4.4 - This chapter focuses on coating on a single particle level. Therefore, the results regarding the coating of isolated aerogel spheres in a modified acoustic levitator setup are discussed. The study is arranged using design of experiment.

- Chapter 4.5 - In this part the coating on a multiple particle level is discussed. The method used for coating on single particle level from chapter 4.4 is validated with the results from the coating on a multiple particle level. Thus, the particle bed is coated in the spouted bed system in order to design the core-shell particles and examine the influence of different process parameters on the coating quality.

- Chapter 5 - The main results of the thesis are summarized in this chapter.

2 Theoretical Background

The following chapter gives the theoretical background to the coating of aerogels. Therefore, first the spouted bed technique is introduced followed by the detailed description of coating mechanisms and applications. Subsequently, the aerogel material group is introduced. Thereby, the preparation methods and resulting material properties are presented. Finally, the state of the art on coating of aerogels is described.

2.1 Spouted bed technology

Spouted bed systems are commonly used to fluidize particles, which cannot be handled in common fluidized beds due to their size or surface properties [Mathur *et al.* [1974]]. The geometry of spouted bed and resulting specific movement of the bed enables fluidization of very large and dense or very light and fine particles [Salikov *et al.* [2015]]. The spouting is induced by a gas or a liquid. Thus, many industrial processes, e.g. drying, coating or agglomeration, can be performed. In this work, a prismatic spouted bed with two adjustable gas inlet slits was used for coating of aerogel particles due to their light weight.

2.1.1 Process description

Spouted beds were first described by Mathur and Gishler in 1955 and developed for drying of moist wheat particles due to their slugging during drying in a conventional fluidized bed [Mathur *et al.* [1955]]. The spouted bed differs from the fluidized bed in the way of introduction of the gas into the system, as shown in Fig. 2.1. In the conventional fluidized beds the gas enters the process chamber equally by the gas distributor plate. In contrast to that, the gas enters the spouted bed system via a slit or a small-sized circular inlet. Thus, the gas inlet cross-section area is small and results in high gas inlet velocities. Additionally, the cross-section area of the apparatus varies with its height. In case of inlet slits, the horizontally flowing gas is deflected and forms a vertical turbulent jet or spout in the middle of the apparatus, taking along the particles. As a result of the decrease of gas velocity and increasing cross-section area of the apparatus with its height a fountain is formed. The particles reach the annulus zone, where they drift toward the walls of the apparatus after reaching the highest point of the fountain and slide back into the process chamber because of gravity. The concentration of the particles in the annulus zone is significantly higher compared to the spout [Gryczka [2009]]. Then, they are entrained by the jet again. Thus, the typical, circulating particle movement inside a spouted bed is formed and schematically shown in Fig. 2.1.

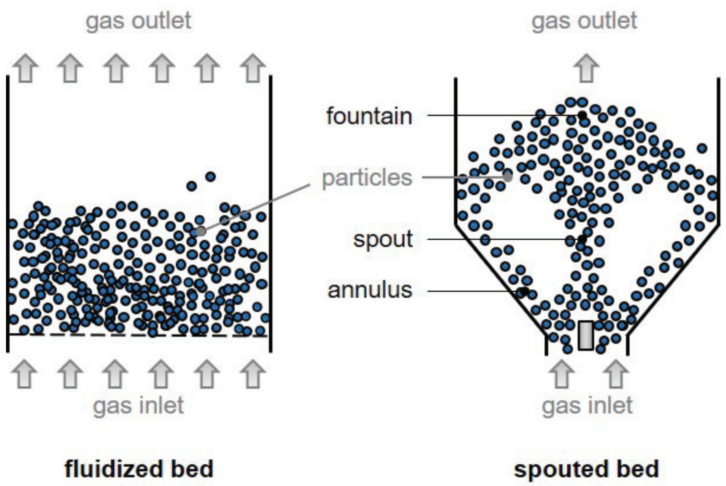

Fig. 2.1: Comparison of the setup of a fluidized (left) and a spouted bed (right).

During coating in the spouted bed the spraying nozzle is placed in the middle of the spout usually in the bottom-spray configuration to spray the coating material in the flow direction. Only few applications with top-spray configurations are reported. The particles come in contact with the droplets of the coating material in the spout zone. The steps characteristic for the coating process, like droplet atomization, wetting, spreading and drying, occur during one circulation cycle of the particles inside of the spouted bed, such that the dry particles with a solidified coating layer are entrained by the gas again. The temperature distribution in the spouted bed varies from that in the fluidized bed. Due to high gas velocities in the spout and intensive particle mixing application of higher temperatures is possible with simultaneously minimized risk of attendance of spots with high temperatures. Thus, spouted bed systems are characterized by excellent momentum, heat and mass transfer properties, and intensive contact between the gaseous and solid phases, leading to short exposure times for the coating liquid and short drying

times [Epstein *et al.* [2011]].
The stability of the spouting process depends on geometry and wall material, gas inlet velocity, particle properties and static bed height. Depending on the geometric aspects, different types of spouted beds are reported: axisymmetric, asymetric and slot-rectangular. Additionally, the flow pattern of the spouted bed can be stabilized by inserting two draft plates [Pietsch [2019]]. For prismatic spouted bed with two inlet slits the gas velocity can be adjusted by the height of the slits. For example, a collapse of the bed or a blockage can be avoided by an instantaneous decrease of the slit height resulting in an increase of the gas velocity [Salikov *et al.* [2015]].

2.1.2 Regime maps

The stability of spouting can be expressed in so called regime maps for a defined apparatus geometry and particle type. The regime map of Salikov *et al.* [2015] shows the behaviour of particle Geldart type D ($1.8\,\mathrm{mm}$, γ-Al_2O_3) in a spouted bed with a prismatic angle of $60°$ and is presented in Fig. 2.2. In the diagram the particle Reynolds number at the gas inlet Re_{in} is plotted against an inlet-to-bed size ratio H. Both are expressed as follows:

$$Re_{in} = \frac{v_{g,in} d_p \varrho_g}{\eta_g}, \tag{2.1}$$

$$H = \frac{2h}{H_{st}}, \tag{2.2}$$

where $v_{g,in}$ is the gas velocity at inlets, d_p the particle size, ϱ_g the gas density and η_g is the dynamic gas viscosity. H is the ratio between the inlet width of both slits $2h$ and the static particle bed height H_{st}.
According to the diagram at low gas velocities the bed is in a fixed state. With an increase of gas velocity bubbles are formed and a irregular bubbling state occurs. When the gas velocity is further increased the minimum spouting velocity, u_{ms}, is reached and the bed is in a stable state, the so called dense spouting. In this regime a spout is formed and a typical circulating movement of the bed consisting of a spout, a fountain and a dense annulus zone exists. By further increase of the gas velocity the bed becomes unstable. A characteristic deflection of the spout (to the left and to the right) and an accumulation of the bed material to one side of the apparatus resulting in instable static bed height occur. The characteristic flow pattern of a spouted bed disappears and the bed flow structure is random. Salikov *et al.* [2015] described first a second stable operation regime of a spouted bed, the so called dilute spouting. This regime occurs by a further increase of

the gas velocity. The particles in this state are highly dispersed in the apparatus and the characteristic zones are still visible. The dilute spouting is limited by the height of the apparatus due to the risk of particle elutriation and is applicable for low to medium bed masses. The use of a diluted spouting can lead to stable operating conditions during processing of very fine particles. Dilute spouting regime was successfully applied in spray coating of ceramics [Brandt *et al.* [2013]], copper [Eichner *et al.* [2016]] and aerogels with particle sizes in μm-range [Goslinska *et al.* [2019b]]. The apparatus used for both studies was prismatic and consisted of a large free-board zone. The same apparatus is used in this work. A detailed description can be found in chapter 3.6.1.

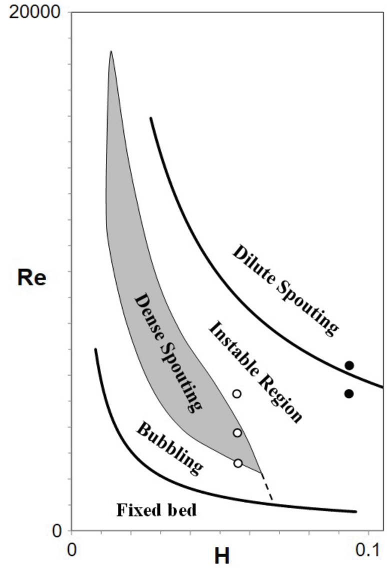

Fig. 2.2: Regime map for of a spouted bed for γ-Al2O3 particles fluidized by air after Salikov *et al.* [2015].

The states occurring during spouting can be additionally described by the pressure drop. A characteristic plot of pressure drop versus gas velocity for a spouted bed is shown in Fig. 2.3. The pressure drop behaviour of a spouted bed differs from that of a common fluidized bed. For a fluidized bed in the fixed bed state the pressure drop increases linearly until the minimum fluidization velocity in reached. At this point the bed becomes fluidized. With beginning of fluidization and further increase of the gas velocity the pressure drop over the bed remains constant. For spouted beds in the fixed bed state an increase of pressure drop with an increasing gas velocity is observed. The first occurring