

FINE INORGANIC PARTICLE DESIGN IN SUPERCRITICAL FLUIDS. SIMULATION OF PARTICLE GROWTH FROM NANOMETER SCALE UP TO MICROMETER SCALE.

Cyril AYMONIER, Sophie DESMOULINS-KRAWIEC, Anne LOPPINET-SERANI,
François CANSELL*

Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB), CNRS-UPR 9048
Université Bordeaux I, 87, Av. du Dr. Albert Schweitzer, 33608 Pessac Cedex, France

*Email: cansell@icmcb-bordeaux.cnrs.fr / Fax : 0033540002761

The process of materials synthesis in supercritical fluid, developed at ICMCB, is based on a chemical reaction (transformation of metal precursors by thermolysis, ammonolysis, red-ox or sol-gel reactions). A wide range of materials can be produced (metals, oxides and nitrides); a well knowledge of the influence of operating parameters allows to tune the characteristics of final particles (size, morphology, composition and structure). However, the developments of materials processing in supercritical fluids are linked to the improvement of the existing numerical tools. Regarding fine particle synthesis, we have proposed a new model of particle growth in supercritical fluids; this model is based on a two steps mechanism: coalescence and then aggregation. The model calculates the evolution of particle size as a function of residence time in the synthesis reactor for metal copper.

INTRODUCTION

Since the 90's research on materials processing in supercritical fluids has received great attention in the scientific community. Today, materials processing represents one of the most promising developments of supercritical fluid technology.

Two main approaches of fine particle synthesis in supercritical fluids exist. The first concerns all the processes based on a physical transformation, ie, the processes for which particle nucleation and growth are induced by a pressure release, the addition of a co-solvent or both [1, 2]. Numerous studies have been performed to try to model the particle growth phenomena with these processes. In the second approach, the nucleation and growth of particles are induced by a chemical transformation of a precursor [3]. An important number of materials has already been synthesized with this process (metals, oxides, nitrides). Beyond the environmental aspect, this new way of materials processing allows a better control of particle synthesis in term of size (few nanometers up to few micrometers), size distribution, morphology, chemical composition (metal, oxide, nitride) and structure [4]. Further developments of this technology are today linked to the capacity to simulate the particle growth mechanism. Indeed engineers need a model which can predict the final particle characteristics as a function of process operating conditions (pressure, temperature, solvent, residence time, precursor concentration,...).

A model was first proposed in our laboratory to calculate the particle size versus media viscosity (pressure, temperature, solvent nature), precursor concentration and residence time [5]. The simulation results are in good agreement with the experimental ones for particle size below a few hundred nanometers. For bigger particles, this model needed an evolution.

In this paper, we propose a new model of particle growth in supercritical fluids based on a two steps mechanism of coalescence and aggregation [6] with model parameters linked to

the crystalline structure of synthesized materials. After the description of this model, its validation is presented with experimental results obtained for metal copper synthesis.

I – MODELLING OF PARTICLE GROWTH IN SUPERCRITICAL FLUIDS

The model formalism is developed for spherical particles synthesis. Liquid-like coalescence and aggregation mechanisms are used to model the particle growth. The other assumptions are reported hereafter:

- The chemical reaction (thermal precursor decomposition) is assumed to be instantaneous. Metal atoms released in the reactive media are homogeneously distributed in the reactor volume,
- Particles are considered spherical at each calculation step,
- Particle growth occurs by binary contacts induced by Brownian movement,
- During the coalescence step, particle volume is calculated starting from the density of the crystalline cell.

The model is divided in two parts as reported in Figure 1. The particle growth begins with a coalescence mechanism up to a particle critical diameter, D_c . At this D_c value, aggregation mechanism takes place for the primary particles.

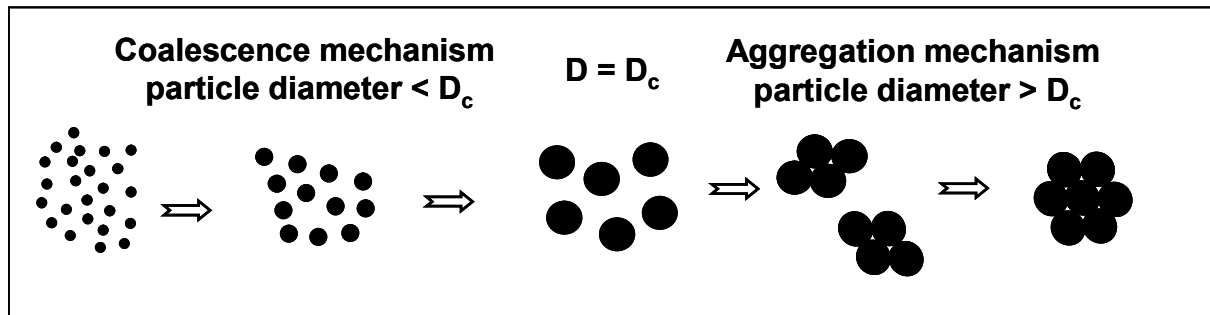


Figure 1: Schematic representation of the particle growth mechanism used in the model

The particles coalesce by binary contact on a time scale shorter than the time between collision events. Each collision between two spherical particles is effective (total coalescence) and gives larger spherical particles. Finally, the numerical model is based on the influence of the diffusion coefficient on the particle size (Stokes-Einstein relation).

During the aggregation mechanism, nanoparticles are aggregating in a disorderly fashion toward a spherical shape (the aggregates are considered spherical). Previous studies about hard spheres packing demonstrated that a packing density of 0.5236 (simple cubic) can be used [7]. Each collision between two spherical aggregates is efficient and gives a larger spherical aggregate with a volume equal to the volume of the two smaller aggregates, so the packing density is considered as a constant during the particle growth.

II – MODEL VALIDATION WITH EXPERIMENTAL RESULTS

Metal copper particles were synthesized in supercritical fluids to validate the model. The experimental set-up is described elsewhere [5]. Copper particles are obtained by thermal decomposition of a copper precursor (copper II hexafluoroacetylacetonate, provided by Sigma-Aldrich and used without any further purification) in a supercritical mixture CO₂/ethanol (80/20 molar ratio). Different residence times were studied. The experimental conditions are presented in Table 1.

Table 1: Experimental conditions of copper synthesis and characteristics of final particles.

Temperature (°C)	225	
Pressure (MPa)	20	
D_c (nm) ^(a)	600	
Experimental results: Mean particle radius versus residence time	Residence time (s)	D_f (nm) ^(b)
	6	50
	24	250
	1800	1240
	3600	1600

(a) D_c is the critical diameter determining the transition coalescence/aggregation mechanism,

(b) D_f is the final mean particle diameter.

The chemical nature and the structure of materials were identified by conventional X-Ray Powder Diffraction (CuK_α radiation). Synthesized metal copper has the following crystallographic characteristics: cubic cell / $a = 3.615 \text{ \AA}$. The particle size and morphology were investigated by scanning electron microscopy, SEM (JEOL 840 microscope) and by transmission electron microscopy, TEM (JEOL 2000FX microscope) for the particles with a size below 500 nm (Table 1).

SEM pictures show spherical aggregates composed of nanoparticles with a size of about tens of nanometers. So the model designed in this paper is based on these experimental observations. In a first step, the nanoparticles grow by coalescence up to a critical size (diameter: D_c), and in a second step, an aggregation mechanism of these nanoparticles induces the formation of nanostructured spherical particles. One of the model parameters (D_c) and the final particle size (D_f) were determined experimentally from microscopy studies (Table 1).

The comparison of simulated and experimental results for metal copper is reported in Figure 2. A close-up of curves is shown for short residence times and shows that the experimental results fit with the simulation of particle growth by taking into account the coalescence mechanism for short residence time. In fact, the difference between the calculated and experimental results increases with the residence time.

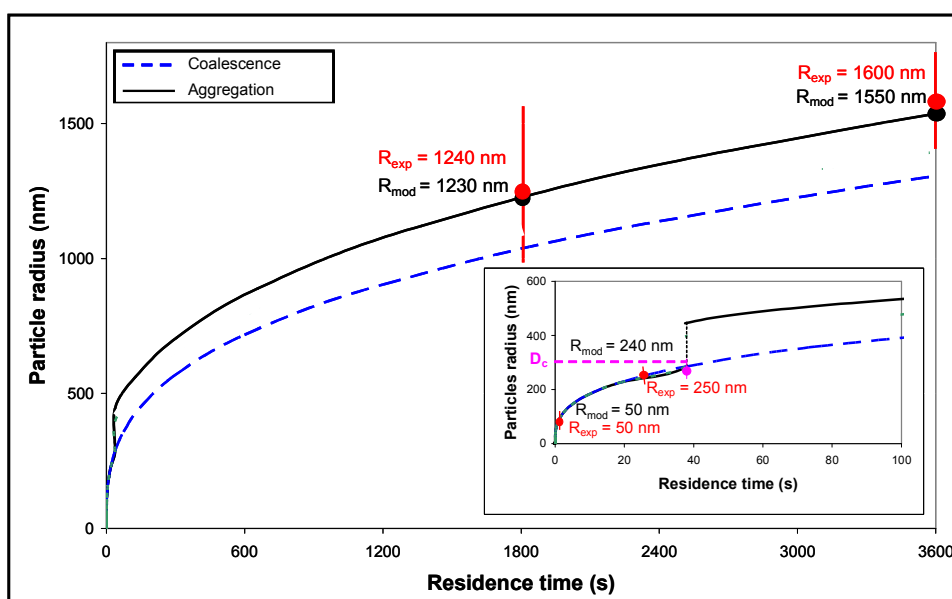


Figure 2: Simulation of copper particle growth versus residence time

The calculated curve with coalescence and aggregation mechanisms presents a discontinuity due to the transition from the coalescence mechanism to the aggregation one at D_c . A good agreement is observed between simulated and experimental results for short and long residence times.

Thus, the model of particle growth in supercritical fluids is validated for metal copper. At a given concentration of metal precursor and media viscosity, the evolution of the particle size can be predicted from a few nanometers up to a few micrometers. Moreover, the model allows equally to simulate the size evolution as a function of precursor concentration and media viscosity.

CONCLUSIONS

The advantage of processes using supercritical fluid as reactive media for producing materials are connected with their unusual physicochemical properties, which cannot be obtained with standard processes. Different operating parameters can be adjusted to tune the characteristics of the final product. The developments of material synthesis processes in supercritical fluids are linked to the improvement of the existing numerical tools.

That is why we have developed a model of particle growth in supercritical fluids; this model is based on a two steps mechanism: coalescence and then aggregation. The model calculates the evolution of particle size as a function of residence time, precursor concentration and media viscosity in the synthesis reactor. The numerical tool was validated with the synthesis of metal copper.

The developed numerical tool is very efficient; the calculations described in this paper show that the particle size can be adjusted from a few nanometers up to a few micrometers by tuning of the process operating parameters.

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