

# SYNTHESIS OF INORGANIC NANOPARTICLES IN SUPERCRITICAL FLUIDS. A SIMPLE MODEL TO PREDICT PARTICLE SIZE

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## ABSTRACT

One of the most promising developments of supercritical fluid technologies concerns today the field of inorganic, hybrid and organic materials processing. Two well known ways are generally associated to materials processing in supercritical fluids: the first way with processes based on a physical transformation (RESS, SAS, PGSS ... processes) and the second one with processes based on a chemical transformation (thermolysis, red-ox, solvolysis ... reactions).

The process of materials synthesis in supercritical fluids, developed at ICMCB, is based on a chemical reaction which induces the nucleation and growth of inorganic nanoparticles. A wide range of nanostructured materials can also be produced (metals, semiconductors, oxides and nitrides); the knowledge of the influence of operating parameters allows to tune finely the characteristics of final particles (size, morphology, composition and structure). However, the development of materials processing in supercritical fluids is closely linked to the proposition of numerical tools. Regarding fine particles synthesis, we have developed a simple model of particle growth in supercritical fluids.

This proceeding describes an attractive simulation tool based on a simple model to predict the evolution of particle size and particle size distribution depending on the operating parameters. The modeling of the growth of nanoparticles is based on a population balance equation taking into account the phenomena that occur in the reactor: the collision and the coalescence of particles. The developed numerical program has been validated in the case of the nucleation and growth of metal nanoparticles in a supercritical CO<sub>2</sub>/ethanol mixture.

## INTRODUCTION

Today, materials processing represents a promising way of development of the supercritical fluid technology. Speaking about materials processing in supercritical fluids refers mainly to two approaches: i) processes based on a physical transformation and ii) processes based on a chemical one. Processes based on a physical transformation are characterized with a particle formation mechanism induced by a pressure release, the addition of an anti-solvent or both<sup>1,2</sup>. Numerous works have been performed to model the particle growth phenomena with these methods. In the second approach, the nucleation and growth of nanoparticles are induced by a chemical transformation of a precursor<sup>3</sup>. An important number of inorganic nanostructured materials (metals, semiconductors, oxides, nitrides) has already been synthesized with this process for different fields of applications: energy<sup>4</sup>, catalysis<sup>5</sup>, telecommunications<sup>6</sup>, ... Beyond the environmental aspect, this method of materials processing allows

a great control of nanoparticle characteristics in term of size (few nanometers up to few micrometers), size distribution, morphology, chemical composition and structure<sup>3</sup>. Further developments of this technology are today linked to our capacity to model and simulate the particle growth phenomenon. Indeed engineers need a tool which can predict the final particle characteristics as a function of process operating conditions (pressure, temperature, solvent, residence time, precursor concentration,...).

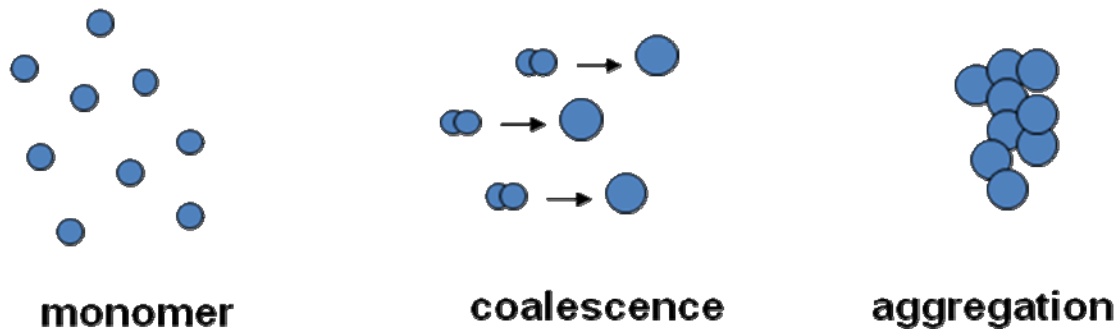
The simulation of the formation of inorganic nanoparticles was just investigated for the synthesis in supercritical water<sup>7</sup>. To estimate the size distribution, the classical nucleation and growth theory was used (precipitation mechanism).

In this proceeding, we propose another growth mechanism; the proposed model of nanostructured particle growth is based on a two steps mechanism: coalescence and aggregation. After the description of the model, its validation is presented with experimental results obtained for the synthesis of metal copper nanoparticles in supercritical CO<sub>2</sub>/EtOH mixture.

## I – MODELLING OF PARTICLE GROWTH IN SUPERCRITICAL FLUIDS

Nucleation and growth of inorganic nanoparticles in supercritical fluids are now studied for the beginning of the 90's. Two main phenomena were experimentally observed to explain the formation of nanostructured metal particles: growth by coalescence and aggregation (Figure 1)<sup>8</sup>.

Thanks to this result, a monodisperse model was adapted to our works from previous studies<sup>9</sup> (synthesis of inorganic particles in flame) to predict the evolution of particle size as a function of the operating parameters.



**Figure 1:** Mechanisms of particle growth in supercritical fluids

In Figure 1, the monomer is a metal atom obtained by the chemical transformation of a metal precursor. This transformation is assumed to be instantaneous. Metal atoms released in the reactive media are homogeneously distributed in the reactor volume.

Two other model assumptions are significant:

- the initial monomers (metal atoms) are stable,
- all aggregates contain the same number of equally sized primary particles.

Furthermore, we consider isothermal conditions during the particle synthesis in the batch reactor.

The developed monodisperse model allows the description of the particle evolution from the variation of three variables: i) the particle concentration  $N$ , ii) the volume of the aggregate  $V$  and iii) the average specific surface area of aggregates  $a$ . The model can be described by the following set of equations.

$$\frac{dN}{dt} = -\frac{1}{2}\beta N^2 \quad (1)$$

Where  $N$  is the number concentration of aggregates per unit of volume of fluid and  $\beta$  is the frequency function for collisions between aggregates.

The growth rate of the aggregate volume  $V$  is proportional to the rate of aggregation.

$$\frac{dV}{dt} = \frac{1}{2} \beta N V \quad (2)$$

The surface area  $a$  increases by coagulation (first term on the right-hand side) and decreases by coalescence.

$$\frac{da}{dt} = \frac{1}{2} \beta N a - \frac{1}{\tau} (a - a_s) \quad (3)$$

The second term on the right-hand side represents the term of surface area reduction due to the coalescence phenomenon.  $\tau$  represents the characteristic sintering time and  $a_s$  is the surface area of the completely fused (spherical) aggregate.

The collision frequency is estimated by the Fuchs interpolation<sup>10</sup>. The characteristic sintering time is calculated with the following equation<sup>11</sup>:

$$\tau = k_0 r_p^4 \frac{T}{T_0} \exp\left(\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right) \quad (4)$$

The lack of knowledge for the pre-exponential term  $k_0$  and the activation energy  $E_a$  implies to fit these parameters with the experimental data. The temperature  $T_0$  ( $T_0=225^\circ\text{C}$ ) is chosen arbitrarily in the range of interest of the study.

## II – MODEL VALIDATION

The model developed in section I was validated with experimental results concerning the formation of metal copper particles in supercritical  $\text{CO}_2/\text{EtOH}$  mixture (80/20 molar ratio). Copper was chosen as model system because its chemistry is well known in the Bordeaux team. The viscosity of the supercritical mixture was given by the Reichenberg correlation, valid for the high pressure fluids and the density was estimated by the state equation of Peng-Robinson.

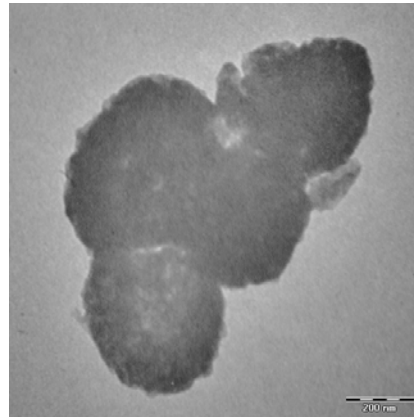
The primary particle diameter is calculated with the model following the relation  $d_p=6V/a$  and compared with the experimental data. Copper particles were obtained by thermal decomposition of a copper precursor (copper II hexafluoroacetylacetonate, provided by Sigma-Aldrich and used without any further purification) in the supercritical mixture  $\text{CO}_2/\text{ethanol}$  according to reference 8. For a temperature above  $200^\circ\text{C}$ , the precursor decomposition can be considered as instantaneous. The experimental conditions and particle size evolution are presented in Table 1.

**Table 1:** Experimental conditions for copper synthesis and particle size evolution

Sample	Operating conditions			Primary particle size (nm)
	P (MPa)	T ( $^\circ\text{C}$ )	t (s)	
Test 1 $m_{\text{precursor}}=150\text{mg}$ $\mu=4.4 \cdot 10^{-5} \text{ Pa}\cdot\text{s}$ $\rho=270 \text{ kg}\cdot\text{m}^{-3}$	20	225	180	37
			900	38
			1800	42
			3600	40
Test 2 $m_{\text{precursor}}=150\text{mg}$ $\mu=4.7 \cdot 10^{-5} \text{ Pa}\cdot\text{s}$ $\rho=307 \text{ kg}\cdot\text{m}^{-3}$	20	200	900	37
			1800	38
			3600	37

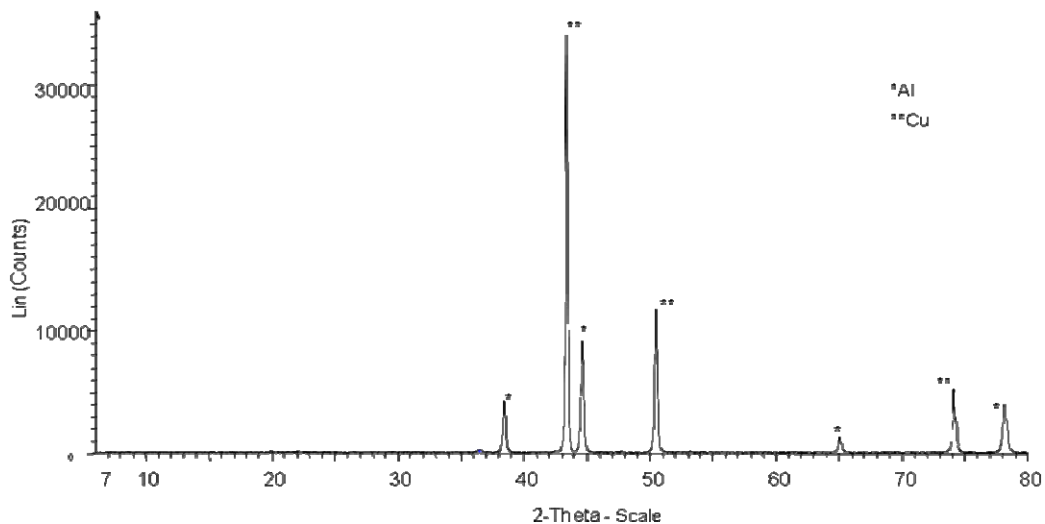
\* Supercritical coordinates of the mixture  $\text{CO}_2/\text{ethanol}$  (80/20):  $P_c = 14.2 \text{ MPa}$ ,  $T_c = 95^\circ\text{C}$

The obtained powders are constituted of spherical aggregates as shown on the scanning electron microscopy (SEM) picture in Figure 2.



**Figure 2:** SEM micrograph of spherical aggregates of copper nanoparticles from test 1

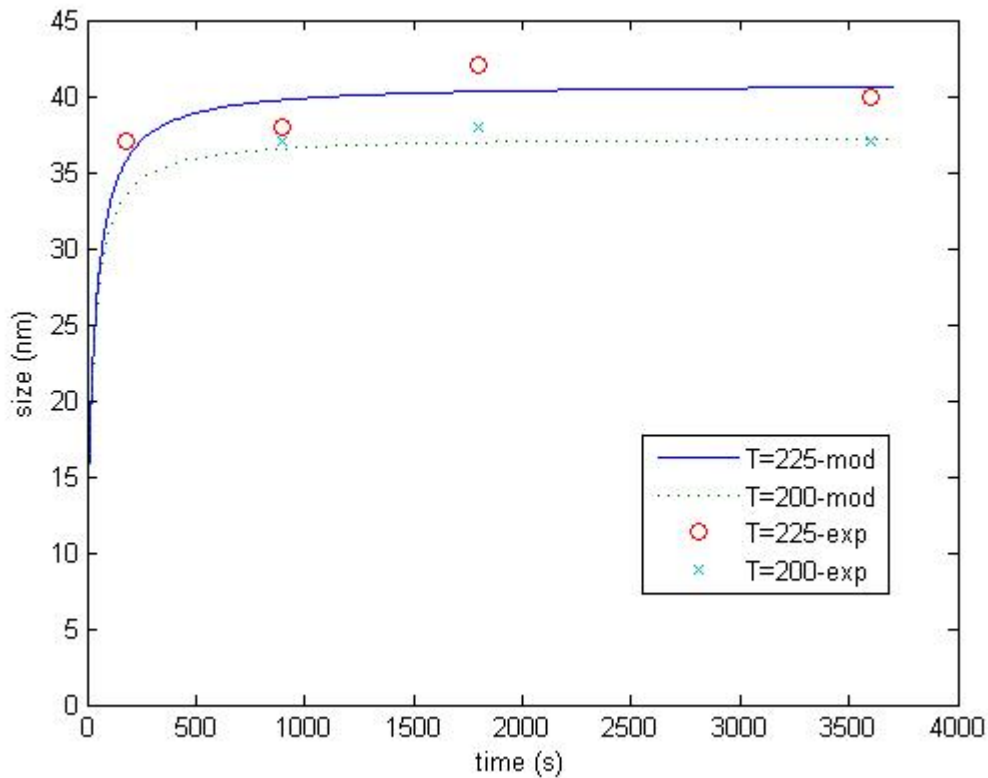
As shown in Figure 2, it is difficult to evaluate by manual counting the primary particle size from microscopy observations. This is why the determination of primary particle diameter was performed with X-Ray Diffraction (XRD) patterns thanks to the Debye-Scherrer equation. The chemical nature and structure of nanopowders were also identified by XRD (Figure 3). Synthesized metal copper has the following crystallographic characteristics:  $a = 3.615 \text{ \AA}$ .



**Figure 3:** X-ray powder diffraction pattern of copper nanoparticles (Test 1)

A Levenberg-Marquardt routine is used to fit the coalescence parameters. The resolution of the system (eq. 1-3) is achieved with the RADAU5 subroutine (Implicit Runge Kutta method of order 5) developed by Hairer<sup>12</sup> particularly well adapted for the stiff problem. The comparison of simulated and

experimental results for the formation of metal copper in supercritical CO<sub>2</sub>/EtOH is reported in Figure 4.



**Figure 4:** Evolution of the primary particle diameter versus residence time

A good agreement is obtained between experimental and calculated results for the model with both coalescence and aggregation mechanisms taken into account. The model of particle growth in supercritical fluids is validated for metal copper. Its validation in other experimental conditions for copper and with other metals is under investigation. Beside the evolution of particle size, the model can calculate the number of primary particles in an aggregate and the number of particles/aggregates.

## CONCLUSIONS

The advantage of processes using supercritical fluid as reactive media for producing inorganic nanostructured materials is connected to the unusual physicochemical properties of supercritical fluids. Different operating parameters can be adjusted to tune the characteristics of the final product in term of size, size distribution, morphology, composition and structure.

To answer to the needs of chemical engineers to develop this technology, we have developed a new model of particle growth in supercritical fluids to predict the evolution of particle size. This model is based on a two steps mechanism: coalescence and then aggregation. The model can calculate the evolution of particle size, the number of primary particles in an aggregate and the number of particles/aggregates. The numerical tool is now validated with the synthesis of metal copper and under investigation for other metals.

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