Kinetically controlled growth of supported NPs through Supercritical Fluid Chemical Deposition

S. Marre[1], A. Erriguible[1], F. Cansell[1,2], F. Marias[3] and C. Aymonier[1,2]*

[1] CNRS, Institut de Chimie de la Matière Condensée de Bordeaux, 87 avenue du Docteur Albert Schweitzer, 33608, Pessac, France

[2] Université de Bordeaux, Institut de Chimie de la Matière Condensée de Bordeaux, ENSCPB, 16 avenue Pey Berland, 33607 Pessac Cedex, France

[3] Université de Pau et des Pays de l'Adour, Laboratoire thermique Energétique et Procédés, rue Jules Ferry, 64075, Pau, France.

*aymonier@icmcb-bordeaux.cnrs.fr

ABSTRACT

The formation of surface nanostructures allows assemblies of materials at different scales, opening routes towards the design of advanced nanostructured materials. Supercritical fluid routes for synthesizing nanomaterials have proved themselves to be efficient methods, especially when surface assembly mechanisms are considered. We demonstrate herein the decoration of surfaces with size-controlled metal nanoparticles (NPs) through the reduction of hexafluoroacetylacetonates complexes [$M(hfac)_x$] with H_2 in supercritical CO_2/alcohol mixtures at low temperature with neither catalysts nor surface prefunctionalization. We investigate the influence of different alcohols – methanol, ethanol and isopropanol – used as cosolvent on the reduction kinetics of $Cu(hfac)_2.H_2O$ in the supercritical CO_2/alcohol/H_2 mixtures. The results are applied to the modeling of the decoration process of silica spheres, used as a model substrate, with copper NPs (5 – 17 nm). The model – using the decomposition kinetics of the precursor - is based on a bi-modal process: (i) an initial homogeneous nucleation in the supercritical media and (ii) a fast heterogeneous growth by coalescence on the surface of silica particles. We present a good agreement between the simulated results and the experimental data showing an advanced kinetically-controlled size of the supported NPs in the range of temperature 100 – 125°C and residence time 0 - 120 min.

I – Introduction

The synthesis of nanomaterials using supercritical fluids has been reviewed several times over the last five years. [1-5] This concept allows developing advanced nanostructured materials, which have attracted wide interest in view of the new properties that can be exhibited, taking advantage of the association of several materials at the nanometer scale (quantum confinement and high surface to volume ratio).[6] In this purpose, more and more studies are nowadays focused on the control of materials properties via modification of their surface.[7] A particularly interesting challenge stands in combining properties of materials at different scales (from bulk properties down to size-depend properties) via the deposition of nano-objects with controlled size and shape on surfaces of bulk materials (supported NPs). These supported NPs can present tremendous interests for catalytic applications.[8]

Supercritical fluids have been successfully used to deposit either organic [9-12] or inorganic [13-15] materials. For instance, high quality metallic films were deposited using Supercritical Fluid Chemical Deposition (SFCD) either on planar substrates,[16] particles,[14] or inside nanoporous templates.[17] The formation of surface nanostructures is achieved through the chemical transformation of metal-organic precursors in supercritical mixtures. The main interest of supercritical fluids is that high nucleation rates can be reached, compared to liquid phase syntheses, leading to narrow size distribution NPs.[18] Previous works have been reported on supported NPs synthesis like gold,[19] platinum,[20] ruthenium,[21] or copper ones.[13]

Authors have previously described a thermodynamic way to achieve control of the size.[20,22] Depending on the conditions in use, it is possible to tune the amount of metal-organic precursors adsorbed onto the surface of carbon nanotubes, or carbon aerogels, prior to their reduction. The transformation of this absorbed precursor by different ways is conducive to the formation of size controlled NPs.

Another way towards the control of the size of the deposited nano-objects consists in controlling the kinetics of the precursor transformation. To achieve such a precise control, one can play on several operating parameters like temperature and residence time, but also on the composition of reacting media. In the case of SFCD, supercritical CO_2 (scCO$_2$) is generally used as the main solvent, due to its low critical coordinates ($T_c = 31°C$, $p_c = 7.38$ MPa). Most of the time, a cosolvent is added in order to improve the solubility of the precursor, as well as to increase the overall density of the supercritical mixture. The nature of this cosolvent can strongly influence the kinetics of the metal-organic precursor transformation, as already shown in Chemical Vapor Deposition processes. Indeed, it was reported for the kinetics of copper deposition from the hydrogen reduction of copper hexafluoroacetylacetonate hydrate $Cu(hfac)_2.H_2O$,[23,24] that the use of alcohol cosolvents allows increasing dramatically the copper deposition rate. These results have contributed to demonstrate the interest of alcohols in decreasing the reduction temperature.

In this study, we present a kinetics / modelling study based on the silica@nanoCu model system. By varying cosolvent, temperature and residence time, the reduction kinetics of the precursor and the decoration process of model substrate were determined and modeled.

II – Experimental section

The reduction kinetics of $Cu(hfac)_2.H_2O$ with H_2 in supercritical CO_2 / alcohol mixtures were determined by proportioning the unreacted precursor after the reaction took place in a high pressure / high temperature experimental set-up described elsewhere.[25] In a typical experiment, a high pressure / high temperature stirred reactor is first loaded with an alcohol solution containing the precursor and further pressurized with hydrogen and CO_2 (final molar composition: CO_2/Alcohol/H_2: 90/5/5, typical concentration of precursor is 10^{-3} g/g of solvents). The mixture is stirred and heated to the desired conditions ($100 < T < 150°C$) using an external heating element surrounding the reactor, while the experimental conditions are followed using a pressure sensor and a thermocouple placed inside the reactor. After a given residence time, the reactor is depressurized and the alcohol solution is recovered.

The supercritical coordinates of the CO_2 / alcohol mixtures versus the molar percentage of CO_2 were estimated by the Equation of State (EoS) of Peng-Robinson, and additional visual checking using a sapphire high pressure / high temperature reactor was performed since the addition of H_2 can modify the critical coordinates of the system,[26] showing homogeneous supercritical phase in the working conditions.

The proportioning of the unreacted precursor was performed using UV-Visible spectroscopy (Cary 1C UV-visible spectrophotometer apparatus), from the absorption band attributed to charge transfer between the ligand and the metallic center ($\lambda = 227$ nm).[27] Several tests were performed with the different systems by varying the temperature (100 - 150°C) and the residence time (0 – 120 min) in order to determine the reduction kinetics.

The synthesis of silica-supported copper nanoparticles were performed for temperatures ranging from 100 to 125°C by dispersing silica spheres in the reaction media. The mean sizes of the obtained copper nanoparticles were measured from TEM pictures.

III - Results

III-1- Reduction kinetics of $Cu(hfac)_2.H_2O$ in supercritical media

Considering that both alcohol and H_2 are in large excess compared to the precursor (molar ratio $> 10^3$), the order of the reaction with respect to these reactants can be assumed to 0, therefore the disappearance of the copper precursor can be written as:

$$\frac{d[Cu(hfac)_2.H_2O]}{dt} = k_{app}.[Cu(hfac)_2.H_2O]^a \text{ , with: } k_{app} = -k_0.\exp\left(\frac{-E_a}{RT}\right) \tag{2}$$

Where a is the order of the reaction with respect to the precursor, k_0 is a constant, R is the perfect gas constant (8,314 J.K^{-1}.mol^{-1}), E_a is the activation energy of the reaction (in J.mol^{-1}) and k_{app} the appearing kinetic constant. From this equation, for each temperature and each alcohol cosolvent the k_{app} were determined at different temperatures (Table 1). Using the obtained values of k_{app}, we have determined the activation energy of the reaction E_a, for each alcohol (Table 1).

Table 1: *Kinetics constants of the reduction of Cu(hfac)$_2$.H$_2$O with H$_2$ in supercritical CO$_2$ / alcohol media at different temperatures and values of the activation energy for each of the three alcohols.*

	T(°C)	Methanol	Ethanol	Isopropanol
k_{app} (10^{-3} min^{-1})	100	2.2 +/- 0.1	1.1 +/- 0.3	0.2 +/- 0.1
	120	11 +/- 0.8	4 +/- 0.2	2.1 +/- 0.1
	130	15 +/- 0.7	6.5 +/- 0.5	3.1 +/- 0.1
	150	31 +/- 1	24 +/- 0.6	11 +/- 0. 4
E_a (kJ.mol^{-1})		69 +/-12	80 +/- 9	104 +/- 15

The activation energy required to reduce Cu(hfac)$_2$.H$_2$O is lower when MeOH is used as cosolvent (69 kJ.mol^{-1}) compared to EtOH or iPrOH (80 kJ.mol^{-1} and 104 kJ.mol^{-1}, respectively) (Table 1), showing the nature of the alcohol strongly influences the value of the kinetics constant. First, the use of MeOH as cosolvent leads to larger values of k_{app} than EtOH or iPrOH (Table 1). Note also that the use of isopropanol allows tuning the value of the kinetics constant of two orders of magnitude ($10^{-4} < k_{app} < 10^{-2}$ min^{-1}) by adjusting the temperature in the range 100-150°C, allowing to obtain a precise control on the reduction of Cu(hfac)$_2$.H$_2$O. Starting from these results, we have chosen to use this last supercritical mixtures to decorate the surface of silica spheres with copper nanoparticles by reducing Cu(hfac)$_2$.H$_2$O with H$_2$ in the presence of silica particles dispersed in the reaction medium. This choice is supported by the fact that iPrOH, as a cosolvent, leads to fine mastering of the reduction kinetics, allows controlling precisely the nucleation rate, which is an important parameter for the design of supported nanostructures. Note that the presence of silica spheres inside the reaction media does not influence the reduction rate,[13] letting us assume a homogeneous nucleation mechanism.

III-2- Synthesis of copper NPs supported on silica spheres

Dispersing silica particles inside the reaction medium during the reduction of Cu(hfac)$_2$.H$_2$O leads to supported copper NPs. Figure 1 shows typical TEM pictures of copper NPs supported on silica, with either 500 nm or 170 nm silica particles (Figure 1-a and 1-c, respectively). It can be noticed that the copper NPs are spherical and well distributed onto the whole surface of silica particles (Figure 1b).[13]
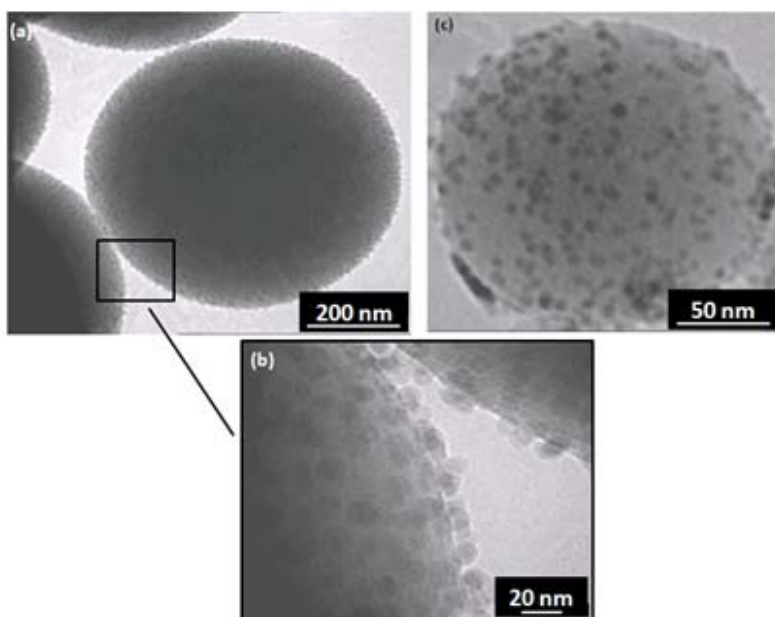
Figure 1: *(a) TEM pictures of a 500 nm silica sphere decorated by copper nanoparticles using the reduction of Cu(hfac)$_2$.H$_2$O with H$_2$ in supercritical CO$_2$/iPrOH media (T = 150°C, 120 min). (b) enlargement of (a). (c) TEM pictures of a 170 nm silica sphere decorated by copper nanoparticles (T = 115°C – 60 min).*

The characteristic size, of the different synthesized materials (SiO$_2$@nanoCu) are summarized in Table 2. The size of copper NPs (d$_{Cu}$) varies from 5 to 17 nm depending on the temperature and the residence time. At constant residence time, the higher the temperature, the larger the diameter of copper NPs. A large difference is observed between the size of nanoparticles synthesized at 100°C (5 nm) and at 150°C (16 nm) (Table 2). At constant temperature, the NPs diameter increases with increasing residence time. These results make one prove of a kinetic control of the size of the Cu NPs.

Table 2: *Experimental conditions and mean diameter of the copper NPs measured from TEM pictures.*

Sample	p (MPa)	T (°C)	R$_t$[a] (min)	d$_{Cu}$ (nm)
1	20	100	60	5 ± 2
			90	6 ± 3
			120	9 ± 5
2	22	115	60	10 ± 5
			90	12 ± 5
			120	16 ± 6
3	23	125	60	11 ± 5
			90	14 ± 6
			120	17 ± 5

[a] R$_t$ is the residence time.

Another key point of surface nanostructuration is the amount of coverage. This study has shown that the main parameter for tuning the amount of coverage of the silica particles with copper NPs is the mass ratio Cu(hfac)$_2$.H$_2$O / silica spheres.
In order to measure the amount of coverage of SiO$_2$@nanoCu spheres, a specific method based on the AFM technique was developed. SiO$_2$@nanoCu particles were scanned by AFM, allowing obtaining topographic profiles of the surface. Using an image analysis software, the average amount of coverage of the surface can be measured. Additional manual counting using TEM pictures were performed in order to confirm the AFM approach. An increase of r$_m$ induces an increase of the amount of coverage. In the first part of the curve (mass ratio up to 20), the variation is almost linear. Then, the amount of coverage tends to a limit at approximately 80%. This is accompanied by the apparition of aggregates of copper NPs inside the recovered solution.

We proposed a mechanism to explain the design of the surface of silica particles with copper NPs; a homogeneous decomposition of the precursor leading to the formation of small copper nuclei made of few atoms. Then, these primary particles deposit onto the surface of silica spheres by binary contact, and finally the growth takes place directly on the surface of silica particles by coalescence of the deposited nuclei. Starting from this assumed mechanism, we have developed a model based on a two steps mechanism.

III-3- Modeling the deposition process

We have used a bimodal model [28] to predict the evolution of the mean size of the supported copper nanoparticles as a function of R_t and T. This model allows taking into account the coalescence and the aggregation mechanisms and suits well for the case of very low precursor decomposition. The bimodal model is in very good agreement with the complete sectional model and requires the same level of computation time that the simple monodisperse model. This model is composed of two discrete monodisperse modes used to represent the particle size distribution: a size fixed nucleation mode (mode 1) and a moving accumulation mode (mode 2). The size fixed nucleation mode accounts for the introduction of newly generated particles (*i.e.* the generation of nuclei due to the precursor decomposition) and the moving accumulation mode characterizes the particle growth by coagulation and coalescence.

The details on the calculations is given elsewhere[25] The model was compared to the experimental results concerning the formation of metal copper particles on the surface of silica spheres in supercritical CO_2 / iPrOH mixture (90/5 molar ratio) (From Table 2). Figure 3 represents the evolution of the primary copper particle size as a function of residence time and temperature.
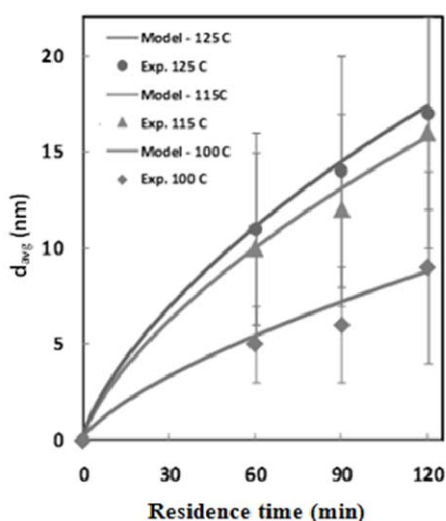
Figure 3: *Evolution of copper primary particle size versus residence time [from ref 25]*

A good agreement is obtained between experimental and calculated primary particle size for the model including both the coalescence and the aggregation mechanisms taken into account. The proposed mechanism for the silica sphere decoration process (*i.e.* homogeneous nucleation followed by heterogeneous growth) is confirmed in the studied conditions. However, it might not be suitable anymore for unexplored conditions, in particular for temperatures above 150-175°C, where there is a competition between two decomposition processes of the precursor (reduction by H_2 / alcohol and thermolysis). This would indeed change the decomposition kinetics and thus the parameters of the model.

In the studied conditions, the first mode (homogeneous nucleation in the reaction media) is the limiting step of the process, which control the number of nuclei released in the reaction media. Since this is directly dependent on the precursor transformation kinetics, these model results clearly show the surface decoration of materials is a kinetically-controlled process.

Conclusion

Materials Science requires efficient methods of synthesizing materials with controlled size, morphology, composition and structure. By using supercritical fluids as a reaction media, material characteristics can be successfully tuned and improved, thus meeting these requirements.

We have demonstrated the alcohol-assisted decoration of silica spheres by copper NPs with a kinetic control of the copper NPs size. This is achieved at low temperature (100 - 125°C) using isopropanol as cosolvent, which allows tuning the reduction kinetics of the precursor by two orders of magnitude (k = 2.2 10^{-4} – 1.1 10^{-2} min^{-1}), compared to methanol or ethanol. A bimodal model was used to predict the size of the obtained copper nanoparticles. This takes into account both the introduction of newly generated nuclei from the precursor decomposition, and the particle growth on the surface of the silica spheres by

coagulation and coalescence. This model, developed for low temperature decomposition of the precursor, fits well with the experimental data obtained and can be applied to other kind of materials nanostructuration. This work demonstrates a new way for controlling the size of supported NPs, which is an important parameter for applications like catalysis, where the specific surface is a critical factor.

As an example, this fundamental approach was applied to the nanostructuration of Mg particles with metal NPs with a real improvement of the properties of hydrogen storage.[29]

References

[1]   Aymonier,C. Loppinet-Serani, A. Reverón, H. Garrabos, Y. Cansell, F. J. Supercrit. Fluids 38 (**2006**) 242.
[2]   Reverchon, E. Adami, R. J. Supercrit. Fluids 37 (1) (**2006**) 1.
[3]   Cansell, F. Aymonier, C. Loppinet-Serani, A. Curr. Opin. Solid State Mater. Sci. 7 (**2003**) 331.
[4]   Holmes, J.D. Lyons, D.M. Ziegler, K.J. Chem. – Eur. J. 9 (**2003**) 2144.
[5]   Cansell, F. Aymonier, C. J. Supercrit. Fluids 47 (**2009**) 508.
[6]   Rotello, V.M. Nanoparticles: building block for nanotechnology, Springer, **2003**.
[7]   (a) Rieter, W.J.; Taylor, K.M.L.; Lin, W. J. Am. Chem. Soc. 129 (**2007**) 9852, (b) Rampazzo, E.; Brasola, E.; Marcuz, S.; Mancin, F.; Tecilla, P.; Tonellato, U. J. Mater. Chem. 15 (**2005**) 2687.
[8]   (a) Volbaek, B.H.; Janssens, T.V.W.; Clausen, B.S.; Falsig, H.; Christensen, C.H.; Norskov, B.S., Nanotoday, 2(4) (**2007**) 14. (b) Astruc, D. Nanoparticles and catalysis, Wiley, **2007**.
[9]   Reverchon, E.; Adami, R. J. Supercritical Fluids 37 (**2006**) 1.
[10]   Reverchon, E. J. Supercritical Fluids 15 (**1999**) 1.
[11]   Jung, J.; Perrut, M. J. Supercritical Fluids 20 (**2001**) 179.
[12]   Shariati, A.; Peters, C. Curr. Opinion in Solid State Mater. Sci. 7 (**2003**) 371.
[13]   Marre, S.; Cansell, F.; Aymonier, C. Nanotechnology 17 (**2006**) 4594.
[14]   Pessey, V.; Garriga, R.; Weill, F.; Chevalier, B.; Etourneau, J. ; Cansell, F. Ind. Eng. Chem. Res. 39(12) (**2000**) 4714.
[15]   Aymonier, C.; Elissalde, C.; Reveron, H.; Weill, F.; Maglione, M.; Cansell, F. J. Nanosci. Nanotech. 5(6) (**2005**) 980.
[16]   Blackburn, J.M.; Long, D.P.; Cabañas, A.; Watkins, J. Science 294 (**2001**) 141.
[17]   O'Neil, A.; Watkins, MRS bulletin, 30 (**2005**) 967.
[18]   Marre, S.; Park, J.; Rempel, J.; Guan, J.; Bawendi, M.G.; Jensen, K.F. Adv. Mater. 20 (**2008**) 1.
[19]   Zhang, Y.; Erkey, C. J. Supercritical Fluids, 38(2) (**2006**) 252.
[20]   Bayrakceken, A.; Kitkamthorn, U.;Aindow, M.; Erkey, C. Scripta Materialia, 56 (**2007**) 101.
[21]   Zhang, Y.; Kang, D.; Aindow, M.; Erkey, C. J. Phys. Chem. B, 109(7) (**2005**) 2617.
[22]   Zhang, Y.; Cangul, B.; Garrabos, Y.; Erkey, C; J. Supercrit. Fluids, 44(1) (**2008**) 71.
[23]   Chiang, C.; Miller, T.; Dubois, L. J. Phys. Chem. 97 (**1993**) 11781.
[24]   Jain, A.; Kodas, T.; Corbitt, T.; Hampden-Smith, M. Chem. Mater. 8 (**1996**) 1119.
[25]   Marre, S. Erriguible, A. Perdomo, A. Cansell, F. Marias, F. Aymonier, C. J. Phys. Chem. C, 113 (**2009**) 5096.
[26]   Ke, J.; Han, B.; George, M.W.; Yan, H.; Poliakoff, M. J. Am. Chem.. Soc., 123 (**2001**) 3661.
[27]   Lussier, L.; Sandorfy, C.; Goursot, A.; Penigault, E.; Weber, J. J. Phys. Chem, 88 (**1984**) 5492.
[28]   Jeong, J.I.; Choi, M. J. of Aerosol Sci., 34 (**2003**) 965.
[29]   a) Bobet, J.L. Aymonier, C. Mesguich, D. Cansell, F. Asano, K. Akiba, E. J. Alloys Compd., 429 (**2007**) 250; b) Denis, A. Sellier, E. Aymonier, C. Bobet, J.L. J. Alloys Compd. (**2008**), doi: 10.1016/j.jallcom.2008.09.016.