

METALLIC COATING OF PARTICLES USING SUPERCRITICAL FLUID CHEMICAL DEPOSITION

Samuel Marre^{a,b}, Cyril Aymonier^a, Christine Marraud^b and François Cansell^{a*}

^aInstitut de Chimie de la Matière Condensée de Bordeaux [ICMCB], CNRS—UPR 9048, Université Bordeaux I, 87 Av. du Dr. Schweitzer, 33608 Pessac Cedex, France

^bSociété Nationale des Poudres et Explosifs - Matériaux Energétiques [SME], rue gay lussac, 33167 Saint-Médard-en-Jalles cedex, France

*E-mail: cansell@icmcb-bordeaux.cnrs.fr / Fax: 05.40.00.27.61

Through Supercritical Fluid Chemical Deposition (SFCD), spherical silica particles were coated with copper nanoparticles (5-20 nm). The elaboration process is based on the reduction of metallic precursors by hydrogen in supercritical CO₂/iPrOH mixture in a range of temperature between 100 and 150°C at about 24 MPa.

INTRODUCTION

Design of new nanoparticle architecture is today a real challenge in materials science owing to the potentiality of development for new multifunctional devices. Nanomaterials exhibit interesting intrinsic properties, which can be different of those of bulk materials due to size effect, such as optical, magnetic or electrical properties. These properties can be modified with an adapted coating [1-3]. Consequently, numerous processes are developed for the synthesis and the functionalisation of nanoparticles, in particular using organic or inorganic coatings. In this context, controlled deposition of metal nanoparticles on a support (nano- and micro-particles, integrated devices, etc...) exhibits a considerable interest.

In addition to the conventional techniques (CVD, PVD, etc.), Supercritical Fluid Chemical Deposition (SFCD) is an interesting way to coat particles with metallic films or nanoparticles. Many studies can be found in the literature on this subject mainly with CO₂ as solvent (environmentally friendly, cheap, low critical coordinates, etc.). This process consists in dissolving hexafluoroacetylacetonates precursors (M(hfac)_x) in a supercritical media, in which the particles to be coated are in suspension. Then, the metallic precursors are chemically transformed to give the subsequent metal that deposits onto the particles surface. Two kinds of chemical transformation are studied [4]: (i) thermolysis reaction [5,6] and (ii) redox reaction with reducing agent [7-11].

Metal deposition through precursor thermolysis has already been studied in our team [5,6]. Nickel particles and samarium cobalt particles of few micrometers have been coated by thermal decomposition of Cu(hfac)₂ dissolve in a CO₂/EtOH mixture. This coating process leads to a nanostructured shell of copper on the particle surface.

Metal deposition through reduction in supercritical fluids should be an interesting competing method. It has been shown indeed that the presence of hydrogen during the deposition of copper and nickel films onto substrates (nanoporous structures, nanowires, Si wafers, polymer surfaces, etc.), permits a softer reduction. Thus, the films are less polluted by precursors

residues [7,8]. The classical reduction temperatures lie between 70°C and 250°C, depending of the metal that is deposited and occurs preferentially on metallic substrates [10]. However, the deposition temperature remains still high for metals like copper (up to 250°C). Moreover, none of these works deal with the reduction of metal precursors by H₂ in presence of an alcohol, whereas it has been demonstrated by Bocquet *et al.*, that the decomposition temperature of the M(hfac)_x can be decreased of approximately 30°C in the presence of an alcohol [12].

In these conditions, the coating of silica particles, used as a model substrate, by copper nanoparticles using the SFCD process is reported here. In order to obtain a low temperature for the synthesis of metallic nanoparticles without a metal catalyst like palladium, the reduction of M(hfac)_x by H₂ in a supercritical mixture CO₂/iPrOH (95/5 molar) is presented.

1/EXPERIMENTAL SECTION

The deposition of copper nanoparticles was performed in a high pressure high temperature stirred reactor of 60 cm³ made of 316 stainless steel. A heating element surrounding the reactor, coupled to a thermocouple, allows to control the temperature, while a pressure sensor placed on the top of the reactor gives informations on the internal pressure (Figure 1). The initial silica particles have an average size of 500 nm (purchased from Alfa Aesar). Hydrogen and CO₂ gases (purchased from Air Liquide) were used as received without any further purification. Isopropanol and Cu(hfac)₂.H₂O were purchased from Aldrich.

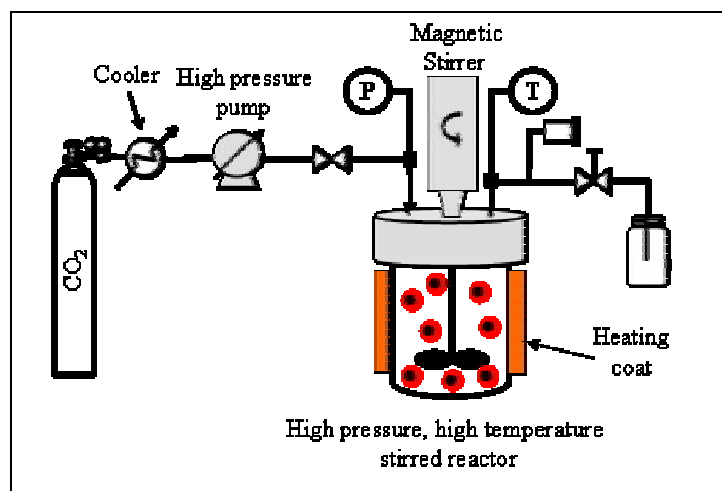


Figure 1: High pressure, high temperature stirred reactor set-up for the coating of particles in supercritical fluids. P and T are a pressure and a temperature controller, respectively.

In a typical experiment, metal precursors are dissolved in iPrOH and silica particles are thereafter added to this solution and put in suspension using an ultrasonic bath stage of 20 minutes [13]. This colloidal solution is introduced inside the reactor, which is closed, filled with hydrogen and CO₂, and brought to the operating conditions: 24 MPa, 130°C, CO₂/iPrOH (95/5 molar), residence time of 2 hours, and stirrer speed of 500 rpm. Under these conditions, the CO₂/iPrOH mixture is supercritical [14]. The redox reaction occurs inside the reactor, which is maintained at constant pressure and temperature during the experiment. At the end of the experiment, the system is depressurised and the coated particles are collected in the isopropanol at the bottom of the reactor.

The particle size and morphology were investigated by Transmission Electron Microscopy (TEM Jeol 2000FX microscope operating at 200kV). The samples were prepared by

deposition of a drop of the coated particles colloidal solution on a copper carbon grid, followed by evaporation at ambient conditions. Chemical nature of materials was identified by conventional X-Ray Powder Diffraction (XRD - CuK α radiation) and Electron Diffraction (JEOL 2000FX microscope). The cover rate was determined with AFM measurements.

2/RESULTS AND DISCUSSIONS

Figure 2 shows a typical silica sphere decorated with copper nanoparticles (reduction conditions: 130°C, 2 hours).

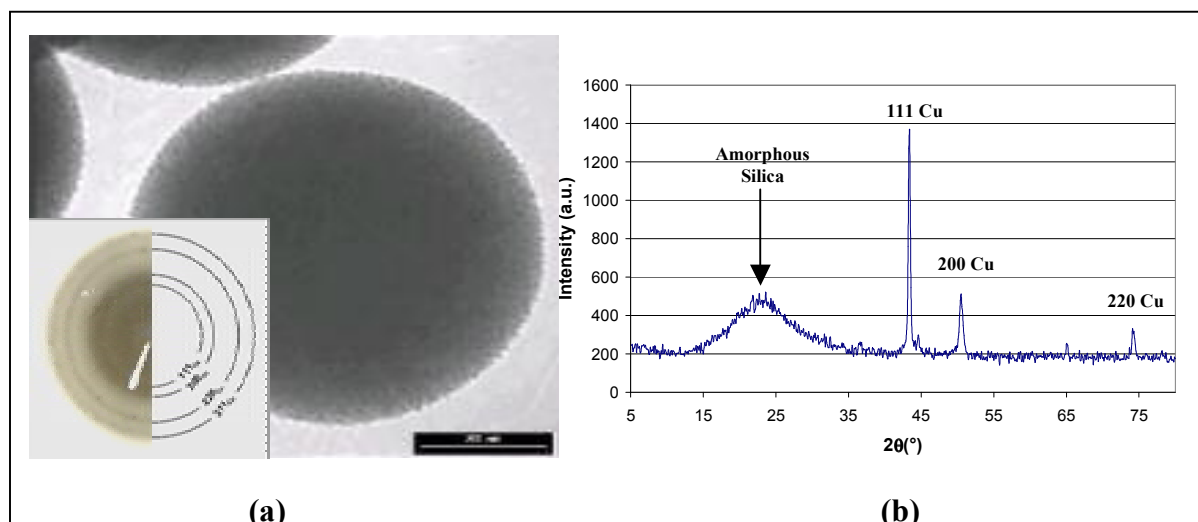


Figure 2: Characterization of silica spheres coated by copper nanoparticles: (a) Electron diffraction pattern and TEM picture, (b) XRD pattern.

The TEM picture (Figure 2a) shows that the copper nanoparticles are spherical and well distributed on the whole surface of silica particle. The cover rate has been calculated using AFM images. By this technique, a cover rate of 80% of the silica particles surface was measured. The average size of copper nanoparticles, measured by manual counting, is 12 +/- 4 nm. The electron and the X-rays diffraction patterns (Figure 2a and 2b) show that the nanoparticles deposited are made of cubic copper ($a = 3.615\text{\AA}$).

The preferential mechanism of coating seems to be a reduction of the metallic precursors by hydrogen to give subsequent metal nanoparticles that deposit onto every available surface in order to minimize their surface energy and cover the silica particles.

The coating was performed at low temperature (130°C). This result shows the interest of alcohols in decreasing the reduction temperature. These molecules seem to act in the reduction process as protons donors and are able to catalyse the reduction, as it was shown by Borgharkar et al. [15] and Kaloyeros et al. [16].

CONCLUSION

Using the SFCD, the decoration of silica particles with copper nanoparticles with a cover rate of 80% and an average size of 12 +/- 4 nm was realised. The reduction of copper hexafluoroacetylacetonate was performed at 130°C without any metal catalyst, a low temperature when compared to results found in the literature between 200 and 250°C.

Further studies have to be performed in order to control the size and the morphology of the copper nanoparticles and the particle cover rate.

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