

# **SUPERCritical FLUID DEPOSITION OF METALLIC NANOPARTICLES OVER MESOPOROUS SUPPORTS**

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**Abstract.** Nanostructured materials have been attracting increased attention for a wide variety of applications due to their superior properties compared to their bulk counterparts. In recent times, in the literature, it can be found attempts to insert transition metals (Co, Cu, Ni, Cr, Ti...) into mesoporous frameworks generally by wet impregnation or co-precipitation showing various drawbacks such as an excessive use of solvents, high energy consumption or costly refining steps. Supercritical fluid deposition (SFD) is an alternative technique, one-pot process, which is able to reduce operational times. An organometallic precursor is dissolved in a supercritical fluid, usually CO<sub>2</sub>, and adsorbed on the mesoporous support. Precursor can then be thermally broken down and/or chemically reduced, and metal or metal oxide nanoparticles are precipitated on the surface and in the pores of the support. Finally, CO<sub>2</sub> is released together with organic byproducts leading to a dry and solvent free material. The excellent properties of scCO<sub>2</sub> (low viscosity and high diffusivity) and their tunability with P and T, make it as an interesting reaction medium for such kind of processes. Moreover, CO<sub>2</sub> is an environmental friendly solvent. This work presents the synthesis and characterization by means of different techniques (SEM, TEM, ICP...) of nanomaterials using SFD. Two different metals, cobalt and nickel, have been deposited into two mesoporous-organized silicas: MCM-41 and MCM-48 respectively. Metallocenes have been used as organometallic precursors. Experimental results have shown an homogenous distribution of metallic nanoparticles showing the convenience of the SFD process.

**Keywords :** Supercritical fluid deposition (SFD), Mesoporous, Metallocenes, Nickel, Cobalt.

## **1. Introduction**

Mesoporous materials with high surface areas and uniform pores structure are currently employed in numerous industrial applications which include adsorption, rectification and catalysis [1,2]

In recent times, various research studies have been focused on increasing the size pores in order to enhance the diffusion of more voluminous reactive molecules towards the active centers. In this way, new materials with pores in the mesoporous range (2-50nm) have been synthesized in order to obtain higher surface areas (500-1500 m<sup>2</sup>) and thus a high adsorption capacity.

For this purpose, MCM-41 and MCM-48 among others, are ones of the most extensively studied mesoporous-silica materials since they were first synthesized by Mobil Corporation in 1992. Both materials contains unidirectional channels arranged in a regular hexagonal pattern in the range 15-100Å.

Moreover, in recent years the interest towards nanostructured materials has grown tremendously [3-6] due to the advantages of the nanoparticles, associated with their small size and, therefore, their large surface area, making them very interesting from the standpoint of catalysts. Many of these properties are related to the manufacture or synthesis process. The main challenge for the development of nanostructured materials is the difficulty of reproducibility, size control and stabilization of nanoscale particles due to their tendency to react and agglomerate.

There are several techniques for depositing metals on substrates, as well as preparing films and supported metal nanoparticles. The commonly employed methods are impregnation, co-precipitation, sol-gel deposition

or chemical vapor deposition. Each one has different advantages and disadvantages; but generally, the main drawback of these methods of synthesis is the control of the particle dimensions, including the size and distribution of particles, as well as the metal content into the matrix of the support. For instance, traditional techniques, such as impregnation or sol-gel, employ liquid solutions causing the agglomeration of the particles and the collapse of the substrate due to the high surface tension. Moreover, the elimination of the surfactant may lead to agglomeration again due to the high temperatures employed.

In that sense, the use of supercritical fluids represents an alternative and a promising method of deposition of metal nanoparticles on the surface of solids and/or inside porous substrates [7,8]. The supercritical reactive fluid deposition (SFD) involves the dissolution of a metallic precursor in a supercritical fluid, generally CO<sub>2</sub>, and subsequent exposure to the substrate. After this impregnation, precursor is reduced and deposition of metal or metal oxide particles takes place over the mesoporous support. This technique takes advantage of the excellent physical properties of scCO<sub>2</sub>, which are easily adjustable with small variations of pressure and/or temperature. Their low viscosity, high diffusivity and zero surface tension achieve better penetrating and wetting of pores than conventional liquid solvents. Furthermore, simple removal from the substrate by depressurization, avoids problems of solvent residues or pore collapse, reducing operational times and carrying out in a one-pot process.

Supported Ni and Co are two of the most deeply investigated transition metal catalysts for different applications, such as catalytic combustion, ammonia synthesis, abatement of NO<sub>x</sub> and especially in reforming processes. Both metals have been identified as ones of the best metals for tar elimination by catalyzing C-C bond breakage and are able to catalyze the decomposition of tars and smaller molecules containing C and O, which is very important for achieving high activities in biomass reactions [9]. In addition, this kind of catalysts shows Brønsted and Lewis acidic sites, enhancing catalytic activity in various reactions such as hydrogenations, isomerization converts or cracking.

## **2. Materials and Methods**

In this section, the synthesis methods of both mesoporous supports by means of template sol-gel technique, and the preparation of the catalysts by supercritical reactive fluid deposition (SFD) are described. Furthermore, the different techniques of characterization used to determine the loading of metal, as well as the distribution of the nanoparticles, location or size are also presented.

### **2.1 Supports synthesis**

Mesoporous supports were synthesized in their spherical shape according to the procedure described by Szègedi [10] and Shiquan [11]. In a typical synthesis process, 2g of n-hexadecyltrimethylammonium-bromide (C16TMABr, ref. H6269, Sigma Aldrich) were dissolved in 42ml of de-ionized water and mixed. Different amounts of absolute ethanol were added to obtain the correct molar composition (48ml to MCM-41 and 18ml to MCM-48). 13ml of aqueous ammonia solution (20 v/v %, ref. 141128, supplied by Panreac Quimilid) were added to this solution and strongly stirred for 15min. Finally, 4ml of tetraethylorthosilicate (TEOS, ref. 333859, Sigma Aldrich) were added drop-wise under continuously stirring to obtain an off-white gel. Then, it was aged for 20h at room temperature; and filtered and washed several times until obtaining a white precipitate with neutral pH. The samples were dried for 16h at 333K and calcined in inert atmosphere up to 773K for 6h, at a heating rate of 2K/min.

### **2.2 Deposition of metal nanoparticles**

Loaded samples with cobalt or nickel were synthesized by supercritical reactive fluid deposition (SFD). In this process, the support and the corresponding organometallic precursor were located inside a high pressure vessel of 100mL volume separated by means of wire mesh. The reactor was heated up to the desired temperature, and CO<sub>2</sub> was pumped into the vessel to achieve the operational pressure. Process was carried out in batch operation, divided in two sequential steps. During the first one, the precursor is dissolved by scCO<sub>2</sub> under optimal operational conditions to favor its solubility, 110 bar and 343K for cobaltocene and 140 bar and 333K for nickelocene, during 1 hour. During this period the dissolution of the metallic precursor in the sc-CO<sub>2</sub> takes places together with its adsorption onto the substrate. The second step involves the thermal decomposition of the organometallic compound. In this stage, temperature is increased to 473K, for 1 hour. Finally, the system was slowly decompressed and the composite materials are recovered from the reactor.

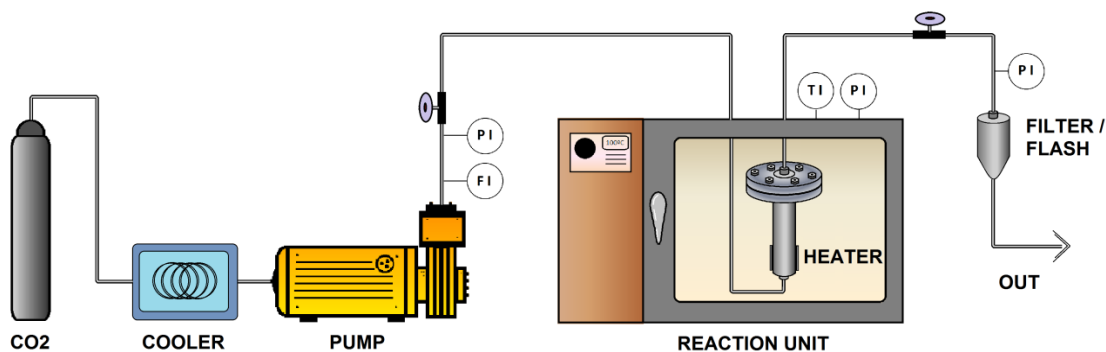


Figure 1. Experimental device

Bis-( $\eta$ 5-ciclopentadienil) cobalt (II), also known as cobaltocene ( $\text{CoCp}_2$ ); bis-( $\eta$ 5-ciclopentadienil) nickel (II), nickelocene ( $\text{NiCp}_2$ ), were chosen as precursors due to their high solubility in  $\text{sc-CO}_2$  [12] and their previous utilization in the deposition of high purity thin films directly on silicon wafers [13].

$\text{CO}_2$  (99.99%) was supplied by Carburos Metálicos; and the organometallic precursors were obtained from Sigma Aldrich:  $\text{CoCp}_2$ , ref. 339164 and  $\text{NiCp}_2$ , ref. N7524.

### 2.3 Catalyst characterization

Different techniques were used to characterize the obtained products:

**BET surface and pore size** were determined by means of nitrogen adsorption/desorption measurements.

**ICP-OES**, Inductively coupled plasma optical emission spectrometry was used to determine the real loading of metal in each product.

**SEM/EDX**, the application of scanning electron microscopy combined with detection by energy dispersive X-ray spectroscopy was performed to analyze the morphology of the surface of the support and determine the chemical composition of the deposited particles.

**TEM-MAPPING**, transmission electron microscopy was employed to verify the organization, morphology and the pore dimensions, as well as to observe the presence of metallic particles within and/or out the matrix of the support.

## 3. Results and Discussion

First of all, it is necessary to emphasize this technique employs high pressures, so it is very important to verify that the regular pore structure of the support remains intact after the deposition. For this purpose, nitrogen adsorption and desorption measurements were used to study the effect of the  $\text{scCO}_2$  over the material; obtaining the results shown in table 1.

Table 1. ICP results and structure parameters of supports and final products

Sample	%Metal <sup>(a)</sup>	BET ( $\text{m}^2/\text{g}$ )	$d_p$ (nm) <sup>(b)</sup>	$d$ (nm) <sup>(c)</sup>	$a_0$ (nm) <sup>(d)</sup>
MCM-41	---	1300	4.6	3.7	4.3
MCM-48	---	1400	2.9	3.6	7.5
Co/MCM-41	3.6	1150	3.9	3.7	4.3
Ni/MCM-48	2.7	Non determined			

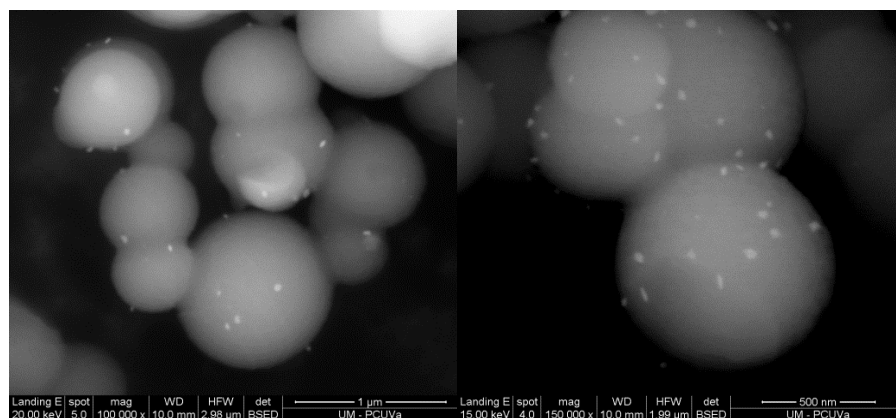
<sup>(a)</sup>Metal w/w% determined by ICP. <sup>(b)</sup>Average pore diameter calculated from desorption branch of nitrogen adsorption isotherms using the BJH model. <sup>(c)</sup>Interplanar distance (MCM-41: $d_{100}$  and MCM-48: $d_{211}$ ). <sup>(d)</sup>Unit cell.

All the samples, the calcined supports and the loaded products, present typical type IV isotherms, characteristic of capillary condensation, which indicates the uniformity of the mesoporous size distribution. Furthermore, BET area of the catalysts are similar to the initial support, showing a slight decrease from approximately  $1300\text{m}^2/\text{g}$  to  $1100\text{m}^2/\text{g}$ . In the same way, the average pore diameter, estimated by BJH, also

suffers an insignificantly lessening from 4.6nm to 3.9nm, showing that the presence of metal and the SFD method do not collapse the structure.

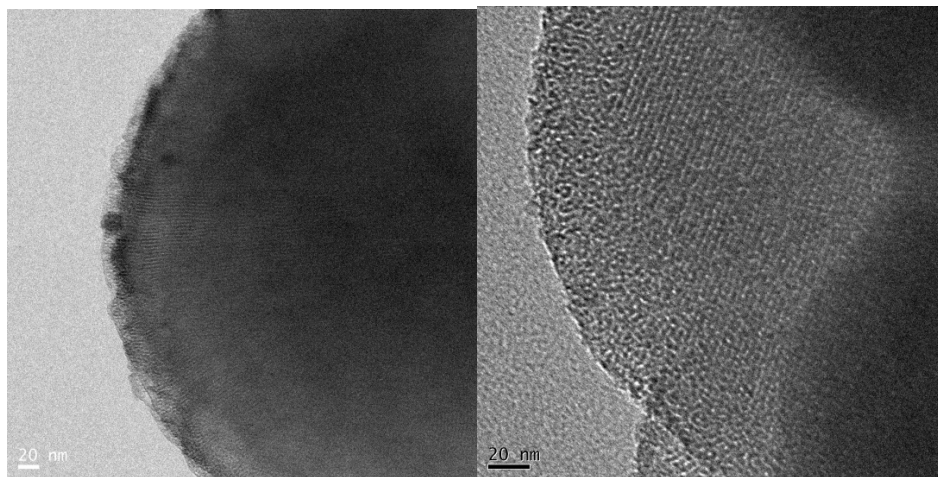
The load of Cobalt in the prepared samples results  $3.6 \pm 0.5$  wt.% that represents a deposition yield of 36% (taking into account the initial amount of precursor located in the reactor). In the case of materials with Nickel, the deposition yield is slightly high (43.3%), and the amount of nickel in the Ni/MCM-48 sample is  $2.7 \pm 0.6$  wt.% determined by ICP-OES.

SEM images (Figures 2 and 3) are performed using the backscattered electron mode (BSE) in order to can observe the deposited metals. The pictures show spherical particles with an average diameter of about 500nm, where appear metallic nanoparticles homogenously dispersed over the surface of the support with sizes less than 20nm.



**Figures 2 and 3.** Metallic nanoparticles dispersed over the surface of the support (Co-MCM-41)

In the TEM pictures (Figures 4 and 5), the intact pore structure can be observed and regular channels in the different supports with various metallic nanoparticles located on the outer surface. In addition, it can be sensed certain gradient of concentration of the metal from the inside of the support (with darker areas) towards the outside (lighter areas).



**Figure 4.** Metallic nanoparticles of Co/ MCM-41 with gradient of metal content;  
and **Figure 5.** Intact pore structure and channels in a Ni/MCM-48 sample.

Figures 6 and 7 show the X-ray mapping results in TEM images for Co/ MCM-41 and Ni/MCM-48 respectively. This mapping confirms the homogenous distribution of the metal into the support.

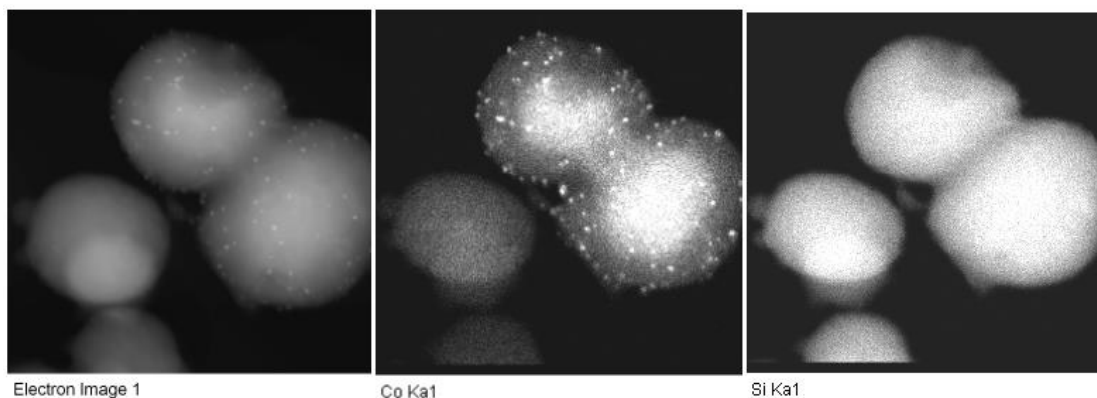


Figure 6. MAPPING of a sample of Co/MCM-41

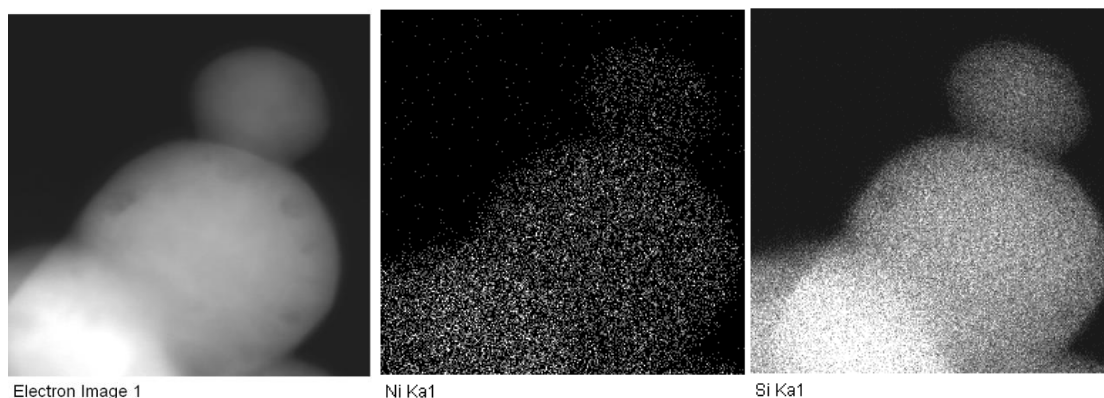


Figure 7. MAPPING of a sample of Ni/MCM-48

#### 4. Conclusions

Supercritical reactive fluid deposition is a reliable technique which led to cobalt and nickel nanoparticles dispersed on the surface of the mesoporous support, MCM-41 and MCM-48, and into the matrix of them, reaching loads up to 3.6 wt. %. The particles have a narrow size distribution with average sizes ranging from 1 to 20nm. Moreover, metal nanoparticles have been homogenously dispersed within the support, as shown by the TEM images. The regular pore structure and surface area of the supports have not been altered because of working with high pressure, maintaining a BET surface superior to 1100m<sup>2</sup>/g.

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