

# Optimization and modelling of the supercritical CO<sub>2</sub> deposition of Co<sub>x</sub>O<sub>y</sub> nanoparticles in MCM41



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## ABSTRACT

Nanocomposites of cobalt oxide on mesoporous silica support (Co/MCM41) have been synthesized by supercritical fluid reactive deposition (SCFRD) using cobaltocene (CoCp<sub>2</sub>) as precursor. The study of adsorption isotherm for CoCp<sub>2</sub> on MCM41 at 70 °C and 11 MPa has revealed an unfavourable adsorbate–adsorbent system with a maximum load of 43 mgCo/gMCM41. Thus, an in situ thermal decomposition of precursor is necessary to obtain higher loadings of active phase. The modelling of the SCFRD process reveals that dissolution is very fast compared to the adsorption of cobaltocene on MCM41, and that Co content is maximum after 1 h of decomposition at 200 °C and 14 MPa. The composite material with 4.3 wt.% Co has a BET surface area of 1034 m<sup>2</sup> g<sup>-1</sup>, a pore size of 3.9 nm and metal nanoparticles of 20–30 nm. This load can be increased by successive batches of 1 h.

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## 1. Introduction

Mesoporous materials, with uniform and tailorable pore dimensions and high specific surface, are currently employed in a number of applications that include catalysis [1,2] and their use as templates for controlling the aspect ratio of quantum-confined nanoparticles and nanowires [3] among others. For many of these applications, it is important that the nanoparticles should be small in size and well-dispersed on a robust support of high surface area. MCM41 is one of the most extensively studied meso-structure materials, since it was first synthesized by Mobil Corporation in 1992 [4]. MCM41 is a mesoporous-silica material that contains unidirectional channels arranged in a regular hexagonal pattern in the range of 20–100 Å. In the recent literature, it can be found attempts to insert metals, such as, Cu, Ca, Mg, Ti, Cr, Mn or Fe into the MCM41 framework, and this incorporation has been generally performed by wet impregnation or co-precipitation [5–10].

Supercritical fluids (SCFs) have been used to incorporate metallic oxide particles and films into a wide variety of supports [11–15]. In the supercritical fluid deposition (SCFD) process, an organometallic precursor is dissolved in supercritical carbon dioxide (scCO<sub>2</sub>), and after impregnation of the support, precursor is

thermally decomposed or chemically reduced, and deposition of metal or metal oxide particles takes place on the mesoporous support. This technique was developed by Watkins and McCarthy [16] and it took advantage of the excellent physical properties of scCO<sub>2</sub>, which are easily adjustable with small variations of pressure and/or temperature. The low viscosity, high diffusivity and zero surface tension of scCO<sub>2</sub> 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, and it can be performed in a one-pot process, reducing operation times [17,18]. The technique can be examined under three main categories: (i) the dissolution of the metallic precursor in the SCF, (ii) the adsorption or sorption of the metallic precursor on the substrate, and (iii) decomposition of the precursor [11,19,20]. According to a recent work [21] that summarizes many methods of insertion of different active phase nanoparticles in mesoporous silica materials, the supercritical fluid reactive deposition (SCFRD) process seems to lead the most homogeneous materials with nanoparticles well-dispersed on the support.

Cobalt is one of the most deeply investigated transition metals for heterogeneous catalytic applications. In the form of supported single element or alloys, cobalt is an interesting active metal for the catalysis of several reactions ranging from catalytic combustion [22,23], steam reforming [24,25], ammonia synthesis [26], Fischer–Tropsch (FT) synthesis [27–30], and abatement of NOx

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[31–33] and CO [34]. Narrowly, (n,m)-distributed single-walled carbon nanotubes (SWNTs) have been obtained with cobalt-incorporated MCM41 (Co/MCM41) catalysts [35,36]. Up to our knowledge, there are few works about the SCFD of cobalt. In this sense, Hunde and Watkins [37] reported the deposition of Co and Ni films directly onto a native oxide of Si wafers and onto TaN and TiN films supported on Si wafers, without the need of a catalytic layer, by H<sub>2</sub> reduction of cobaltocene (CoCp<sub>2</sub>). In this work, dissolution of CoCp<sub>2</sub> in the CO<sub>2</sub> was performed at 70 °C and 11.0 MPa for 1 h and deposition time was 30 min in all cases. Reduction temperature of cobaltocene was varied in the range 285–320 °C and the pressure was modified between 22.0 and 26.0 MPa. No significant deposition was observed below 280 °C and the operational times of the two steps were not varied. Up to now, only a few organometallic compounds on porous support have been studied in scCO<sub>2</sub>. The adsorption equilibrium of [Pd(hfac)<sub>2</sub>] on silica SBA-15 and the influence of the temperature, pressure and density in the process has been examined [38]. The adsorption isotherms of [Pt(CODMe<sub>2</sub>)] on different supports, such as carbon aerogels, silica gel tablets or monolithic silica have been reported [39,40].

Our research group has shown the deposition of 1 and 5 wt.% Co on mesoporous MCM41 and AlMCM41 substrates with supercritical CO<sub>2</sub> at 200 °C and 11 MPa [41]. Due to the promising results obtained, the present work goes deep to the synthesis in order to understand the process and to optimize the operational conditions and model the reactive deposition process with scCO<sub>2</sub>.

Hence, the aim of the present work is to optimize the deposition of cobalt oxide on the MCM41 mesoporous substrate using cobaltocene (CoCp<sub>2</sub>) as precursor and CO<sub>2</sub> as supercritical fluid. For this purpose, three consecutive stages are examined: (i) determination of adsorption isotherms of CoCp<sub>2</sub> on MCM41 support, (ii) study of operational variables: time, pressure and temperature in the SCFRD method of synthesis during adsorption and precursor decomposition stages and (iii) physicochemical characterization of the solids by different techniques such as FTIR spectroscopy, X-ray diffraction (XRD) and inductively coupled plasma (ICP-OES).

## 2. Materials and methods

### 2.1. Organometallic precursor: cobaltocene

Cobalt(II)bis-(η<sup>5</sup>ciclopentadienil), also known as cobaltocene (CoCp<sub>2</sub>) has been used as cobalt precursor in the present work because it is known to be highly soluble in scCO<sub>2</sub> [40] and it has been used in the cobalt deposition of high purity thin films directly on silicon oxide [37]. CoCp<sub>2</sub> was provided by Sigma–Aldrich and used as received.

### 2.2. Synthesis of MCM41 support

MCM41 support was synthesized following the method of Szegedi et al. [42]. A solution of surfactant (C<sub>16</sub>TMABr) was prepared by continuous mixing with de-ionized water and absolute ethanol at room temperature. The pH of the solution was adjusted by adding an aqueous ammonia solution (29 wt.%). Then, tetraethylorthosilicate (TEOS) was added dropwise in a couple of minutes. The molar composition of the resulting gel mixture was TEOS:0.3C<sub>16</sub>TMABr:11NH<sub>3</sub>:144H<sub>2</sub>O:58EtOH.

The obtained support was filtered, thoroughly washed with de-ionized water and dried for 12 h at 60 °C. The template was removed by calcination in flow of air at 550 °C during 6 h.

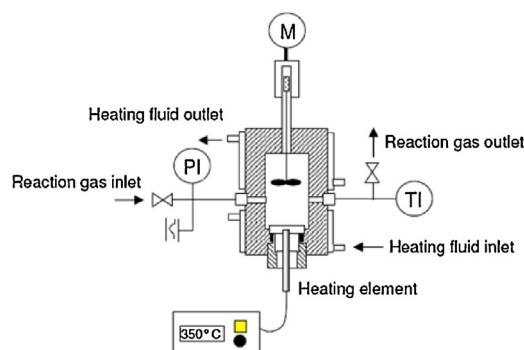


Fig. 1. Flow sheet of the experimental device for adsorption isotherms determination.

### 2.3. Experimental set-up for determination of adsorption isotherms

The determination of adsorption isotherms was carried out in a high pressure reaction chamber. A scheme of the experimental set-up is reported in Fig. 1. The chamber, HP HD300 from Eurotechnica GmbH, is built on SS316-Ti and it has an internal volume of 25 ml, supporting 30 MPa and 150 °C as maximum operating conditions. A magnetic driven agitator (12 VDC with transformer 230 VAC) is installed at the top of the reaction chamber in order to ensure a homogeneous medium. The temperature of the vessel was controlled by means of an electrical jacket (230 VAC; 50/60 Hz) connected to a digital display and NiCr–Ni thermocouple with a ±0.1 °C accuracy, while the pressure inside the chamber is measured by a pressure gauge between 0.1 and 40 MPa.

At the beginning, a known amount of support and precursor are introduced at the bottom of the chamber in two separate perforated containers. The CO<sub>2</sub> is pumped with a dosing pump Milton Roy Dosapro, MILROYAL D (up to 0.6 L/h and 24 MPa) and heated up to operational conditions. Experiments were carried out at constant temperature (70 °C) for 24 h, carrying the amount of precursor at different CO<sub>2</sub> pressures [39,40]. After that, the fluid is slowly depressurized in order to prevent the sweeping along particles and recover the products for further analysis.

### 2.4. SCFRD of CoCp<sub>2</sub> on MCM41

The deposition experiments were carried out in batch process in a home-made high pressure vessel made up of stainless steel with an internal volume of 100 ml. The experimental set-up, given in Fig. 2, operates up to 30 MPa and 400 °C as maximum allowable working conditions. A dosing pump Milton Roy Dosapro (flow rate up to 6.2 L/h and 33 MPa maximum pressures) was used to feed the CO<sub>2</sub> into the reactor.

At the beginning of each experiment, 150 mg of support and 100 mg of organometallic precursor were placed into the vessel, separated by wire mesh to allow the circulation of scCO<sub>2</sub> and avoid their direct contact (Fig. 3). The reactor is equipped with two walls electrical resistances (250 W) placed at the bottom to promote the convective flow of scCO<sub>2</sub>. The process temperature is controlled by a K-type thermocouple located inside the reactor and connected to a PID controller (Desin Instruments 2100 BS) acting on this electrical resistances. A pressure transmitter (ATSA TPR-14/STD) located at the top of the reactor is used for the continuous registration of pressure. Wall temperature is also measured (Fig. 2).

Deposition experiments were carried out in batch operation divided in two consecutive stages. During the first step, precursor is dissolved by scCO<sub>2</sub> and adsorbed onto the support from the fluid medium. Experiments were conducted at 70 °C and 11 MPa in this first stage, and time was varied between 1 and 3 h, in order to study

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