



# Phosphine- and ammonium-functionalized ordered mesoporous carbons as supports for cluster-derived metal nanoparticles



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## ABSTRACT

An ordered mesoporous carbon (OMC) was functionalized with ammonium or chelating phosphine ligands. In both cases, the functionalization procedure started by oxidation by nitric acid treatment, followed by activation of surface carboxylic acid groups with thionyl chloride, then formation of amide bonds with diamines. The pendant amine groups were then either quaternized or further reacted with phosphine. The introduced functions were used as anchors for molecular mixed-metal clusters. These organometallic grafted species could then be thermally transformed into hetero-metallic nanoparticles (NP) embedded within the mesoporous framework. The NP/OMC nanocomposites could find application in hydrogenation heterogeneous catalysis or as electrodes in fuel cells.

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## 1. Introduction

Porous carbons have drawn a widespread attention during the past years in various domains such as energy storage (anodes for Li-ion batteries or double-layer supercapacitors [1–3]), adsorption [4,5] and as catalysts supports [6]. The most used materials in these domains, especially as supports for catalysis, are activated carbons, obtained by pyrolysis and activation of natural species such as wood residues, olive stones or orange skin for instance [7]. This high interest is mainly due to the fact that porous carbons are stable in acidic as well as in alkaline media, they exhibit a high thermal stability and the dispersed catalytic species (noble metals for instance) can be easily recovered by burning away the carbon [8]. Nevertheless, the porosity of activated carbons is very difficult to control and is highly dependent on the raw material used for its production. In addition, they often contain mineral impurities, which could interfere in the catalytic processes, their production is energy-consuming and a high burn-off of the starting material is always present [3,9]. Moreover, activated carbons are essentially microporous, which in heterogeneous catalysis leads to diffusion limitations and even deactivation upon pore blocking by reactants or products. It is known that the length of mass transport can be reduced by about 20 times if the pore sizes increase from microporous to mesoporous. For that

reason, an increased attention has arisen toward the development of synthesis pathways leading to mesoporous carbons, such as carbon xerogels and ordered mesoporous carbons (OMC) [10,11]. During the last years, lots of efforts have been devoted to the preparation of ordered mesoporous carbons, in view of their remarkable structure. Indeed, in addition to their interesting features inherent to the carbonaceous nature of the framework (hydrophobicity, thermal stability, corrosion resistance), their structure can be described as a regular stacking of mesoporous channels with a defined pore width, providing a very homogeneous environment for catalytic sites.

The first preparation of OMC was described in 1999 by Ryo and co-workers (denoted as CMK materials) [12,13]. The strategy involved is based on a nanocasting procedure, where mesoporous silica is used as a sacrificial template. In detail, carbon polymers are formed inside the pores of the mesoporous silica, followed by pyrolysis and removal of the inorganic framework by HF treatment. This route, also called hard-templating, leads to highly ordered mesoporous carbons that are perfect inverted replica of the sacrificial silica. They can be described as a stacking of nano-rods stabilized by pillars and delimiting regular mesoporous voids in-between them. The pore sizes of the carbon thus depend on the pore wall thickness of the silica template, and can be tuned upon choosing the appropriate preparation method of the latter [14]. The preparation of ordered mesoporous carbons by hard-templating was very well reviewed by several authors [15,16]. More recently, soft-templating was proposed as an alternative strategy for the preparation of OMC.

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In this case, the carbon framework is directly created in presence of surfactant molecules in the same manner as for the synthesis of ordered mesoporous silica [11,15,17]. Such a new route is very attractive, since there is space for more flexibility in tuning the pore sizes, the spatial regularity and the surface properties. The structure is also different since the material is made of true tubular mesopores in contrast to the stacking of carbon rods delimiting mesopores, allowing for an increased mechanical stability. Though more elegant, less expensive and less time-consuming, the major drawback of the soft-templating route is the need for a precise control over the interaction between surfactant molecules and growing carbon polymer species and the kinetics of the subsequent formation of the continuous carbon framework. For that reason, the direct syntheses reported are mostly very sensitive to pH and temperature, involve very long durations when prepared in diluted aqueous media [18] and need the evaporation of large quantities of solvents in the case of Evaporation-Induced Self-Assembly (EISA) [19]. Phase separation was also reported as an alternative, but in this case, HCl is used as a catalyst, making this route not adapted when poisoning by  $\text{Cl}^-$  ions has to be avoided, for instance in catalysis [20]. Although promising alternate preparation ways have been proposed recently [21], until now, the hard-templating route remains the most widespread in the application of OMC for energy storage or heterogeneous catalysis.

Ordered mesoporous carbons indeed serve as good starting materials for further modification with catalytically active species. The most widespread is the incorporation of metallic elements (Pd, Ir, Co, Fe, etc.), either during the preparation or via post-synthetic methods. It has been shown that the use of OMC as supports lead to high performance catalysts, due to the better dispersion of the active species and the low pore diffusion resistance [22–27]. It has to be emphasized that the nature of the groups present at the surface of the porous carbons plays a key role for their further application. This important fact has been extensively reviewed by Figueiredo very recently [9]. Porous carbons principally bear oxygenated and nitrogenated surface groups that can be active sites for catalysis, be used either for anchoring catalysts or catalysts precursors, or even serve for a further functionalization of the surface [9,15]. For this latter case, many examples refer to the functionalization with sulfonic acid groups covalently attached to the surface, to produce acidic catalysts used for instance in esterification of organic acids with ethanol or alkylation of aromatic compounds [28]. Finally, surface functionalization with molecules bearing specific functions is especially interesting for anchoring catalytically active compounds, like metal complexes or nanocluster-derived nanoparticles [29,30].

A wide variety of methodologies have been used to introduce metallic nanoparticles within mesoporous carbon frameworks. The synthesis of this type of host/guest materials can be accomplished by two different procedures: either by addition of the metal precursors during the synthesis of the OMC, or by a post-synthetic incorporation of the metal precursors, usually by impregnation. One of the systems that has attracted considerable interest is the Pt/OMC nanocomposite [31–37]. Platinum nanoparticles on mesoporous carbon find applications as sensors or in hydrogenation reactions and electrochemical oxidation of hydrogen or methanol in fuel cells. Beside Pt, other metals, such as Fe, Pd, Ni, Ru and Ag have been loaded onto OMC, introducing magnetic and/or catalytic properties [38–40]. As an alternative to post-synthesis modification, metal precursors can be introduced with or before carbon precursors at the nanocasting stage to produce carbon-based nanocomposites with metals, such as cobalt, titanium, copper, iron, and nickel [41–44]. During carbonization, metal salts or oxides are spontaneously reduced to metal nanoparticles and, though part of the particles is embedded in the walls, their surface still remains accessible. The advantage of this technique is that the

pores of the OMC are not obstructed, but the post-synthesis modification still remains the most versatile and widespread route. Few examples of bimetallic nanoparticles can be found and generally concern association between platinum and ruthenium for fuel cell applications [45–48]. They are usually prepared by impregnation of porous carbon with solutions of the corresponding metal salts.

Heterometallic molecular clusters are ideal precursors for bimetallic nanoparticles of controlled composition. Most of the time, the cluster-derived catalysts are found to be more active and selective than commercial catalysts or their salt-derived counterparts [49,50]. The improvement of selectivity is attributed to the strong metal–metal interaction within heterometallic NPs and to the better dispersion on the surface. Most heterogeneous catalysts based on clusters are used in hydrogenation [50–57] and in Fischer–Tropsch reactions [58,59].

In this paper, we report the preparation of bimetallic nanoparticles supported on an ordered mesoporous carbon. The carbonaceous material was first functionalized with neutral chelating phosphine or charged ammonium groups in order to introduce anchoring points for bimetallic molecular clusters. The grafted clusters were then converted into nanoparticles by gentle thermolysis. To the best of our knowledge, this is also the first example of phosphine-functionalized OMC, which could be used as support for a wide range of catalytically active species, including homogeneous complexes.

## 2. Experimental

All manipulations were carried out under  $\text{N}_2$  using standard Schlenk techniques. The solvents were distilled or degassed before use, stored under nitrogen on molecular sieves, and the obtained products were stored under Ar in a glovebox. The mesoporous carbon, noted Cm, was prepared as a replica of SBA-15 following the route described by Ryoo et al. [12,13]. Functionalized supports, Cm-PPh<sub>2</sub> and Cm-NMe<sub>3</sub><sup>+</sup>, were prepared according to procedures described elsewhere [60]. All mentioned reactants were commercially available and used as received. Triruthenium dodecacarbonyl ( $[\text{Ru}_3(\text{CO})_{12}]$ ) was supplied by Alfa Aesar. Chloro(triphenylphosphine) gold ( $\text{Au}(\text{PPh}_3)\text{Cl}$ ), bis(triphenylphosphoranylidene) ammonium chloride (PPNCl), dichloro(1,5-cyclooctadiene)platinum ( $\text{Pt}(\text{COD})\text{Cl}_2$ ), tetraphenylphosphonium chloride (PPh<sub>4</sub>Cl), ethylenediamine ( $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_2$ ), paraformaldehyde ( $(\text{CH}_2\text{O})_n$ ), methyl trifluoromethanesulfonate ( $\text{CF}_3\text{SO}_3\text{CH}_3$ ) and iron pentacarbonyl ( $\text{Fe}(\text{CO})_5$ ) were supplied by Aldrich. Thionyl chloride ( $\text{SOCl}_2$ ), dicobalt octacarbonyl ( $\text{Co}_2(\text{CO})_8$ ) and tetraethylammonium bromide ( $\text{NEt}_4\text{Br}$ ) were supplied by Acros Organics. Diphenylphosphine (HPPH<sub>2</sub>) and 2-dimethylaminoethylamine ( $\text{H}_2\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_3)_2$ ) were supplied by Fluka. Nitric acid 65% was supplied by VWR and hydrochloric acid 36% by Fisher Scientific.

### 2.1. Functionalization of the mesoporous carbon

#### 2.1.1. Oxidation of Cm to give Cm-ox [61]

The amount of oxygenated functional groups at the surface of the starting mesoporous Cm carbon support was increased by an acid treatment with  $\text{HNO}_3$ . In a typical experiment, 500 mg of Cm were placed in a 100 ml round-bottom flask with 20 ml  $\text{HNO}_3$  1 mol/l or 2.5 mol/l. The mixture was stirred for 24 h at 110 °C (reflux). Then, it was filtered and extensively washed with distilled water until neutral pH. The resulting powder was dried under vacuum at 70 °C during 16 h. The Cm-ox sample oxidized with 1 mol/l nitric acid was selected for the next steps. The surface O/C ratio of this sample was determined by XPS to be equal to 0.125. Based on

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