

# The role of carbon materials as supports for transition metal-based catalysts

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## Abstract

In this communication, a brief overview of the studies developed by the Coordination Chemistry and Catalysis (CCC) Group of Centro de Química Estrutural (Instituto Superior Técnico, Universidade de Lisboa) related to the use of carbon materials as catalysts supports is presented. CCC recent and relevant achievements in the field of carbon supported catalysis are highlighted, focusing on oxidative catalytic reactions.

## Resumen

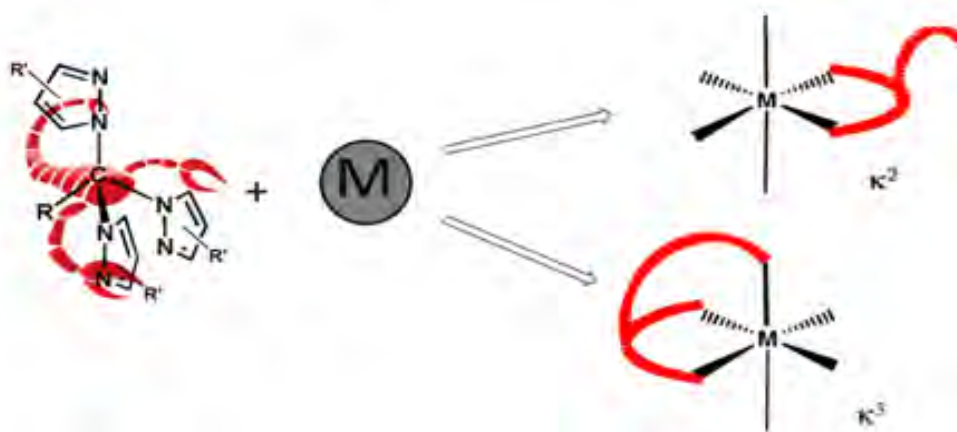
En esta comunicación se divulga una visión general de los estudios que se realizan en el Grupo de Química de Coordenação e Catálise (CCC) del Centro de Química Estrutural (Instituto Superior Técnico, Universidade de Lisboa) correspondiente a el uso de materiales de carbono como soporte de catalizadores. Se destacan los logros más relevantes y recientes del CCC centrados en el campo de la catálisis soportada, en particular en reacciones catalíticas oxidativas.

## 1. Introduction

The interest on carbon materials to be used as supports for catalysts, pioneered at CCC by Luísa

Martins, emerged in 2010 when she met Sónia Carabineiro, from the University of Porto, at the XVI Encontro Luso-Galego de Química held in Aveiro, Portugal.

Luísa Martins was working in homogeneous catalysis mainly for alkane and alcohol selective oxidations, one of the most important processes to produce useful value-added chemical compounds from petroleum-based materials. She designed C-scorpionate tris(pyrazol-1-yl)methane complexes (Figure 1) of several transition metals (e.g., V, Fe, Cu, Ru or Re) [1-17] to act as efficient catalysts for the above reactions. They have been studied with great success and interesting results have been achieved, leading, in most of the cases, to the award of Portuguese patents [13-17] and articles [1-12]. In fact, the facile interchange between bi- and tridentate coordination modes of the poly(pyrazolyl) moieties (Figure 1), changing their denticity during the catalytic reaction, is at the core of the structural and chemical versatility of C-scorpionate complexes and was essential for their catalytic applications. Moreover, the presence of N- and O- donor atoms in C-scorpionate ligands allow their complexes to assist proton-transfer steps, which are believed to be involved in key processes of the oxidation reactions such as the metal-promoted radical generation [18,19].



**Figure 1.** Schematic structure of a tris(pyrazolyl) type scorpionate [R = H, Me, CH<sub>2</sub>OH, CH<sub>2</sub>NH<sub>2</sub>, COOH, CH<sub>2</sub>O(CH<sub>2</sub>)<sub>n</sub>Y (Y = SO<sub>3</sub>, Ph, Py), P(O)(OR)<sub>2</sub>, etc.; R' = H, Me, Ph <sup>t</sup>Pr, <sup>i</sup>Bu, etc.], its common coordination modes to a metal centre (M), and analogy with a scorpion and its attack on a prey. Adapted from [18].

However, although active and selective, the above homogeneous catalysts lack in reusability. The immobilization of a molecular catalyst in an inert support could improve its catalytic activity and allow its easier separation and recycling, which are required conditions in sustainable processes. In particular, the use of carbons as catalyst supports provides unparalleled flexibility in tailoring their physical (surface area and porosity) and chemical

(surface functional groups) properties. Therefore, the combination of the properties of homogeneous complexes with the advantages of heterogeneous systems would be obtained.

By that time, Sónia Carabineiro had already a long experience in the production of various types of carbon materials and in the modification of the nature and concentration of surface functional groups [20-22], which can be used to anchor metal complexes.

She also had also acquired expertise in anchoring procedures [23]. Thus, a collaboration started aiming at producing hybrid materials based on C-scorpionate complexes and testing them as catalysts for important industrial oxidation reactions.

The first supported materials prepared were C-scorpionate iron(II) and gold(III) complexes immobilized in functionalized carbon materials such as activated carbon, carbon xerogel or multiwalled carbon nanotubes, to be applied as catalysts for the peroxidative oxidation of cyclohexane [24,25]. Then, these studies were extended to *i)* other metal complexes, not exclusively C-scorpionates [26-30]; *ii)* other catalytic reactions [26-31]; *iii)* gold nanoparticles [32-35], and *iv)* different nanostructured carbon materials (e.g., graphene oxide, reduced graphene oxide, graphene nanoplatelets, nanodiamonds and nanohorns) [35-37].

In the last approach, in collaboration with Ana Paula Carvalho from Centro de Química e Bioquímica of Faculty of Sciences of Universidade de Lisboa, biomass-derived carbons, obtained from lignocellulosic wastes, were successfully used [30,37]. Recently, in collaboration with José Virgílio Prata from the Chemical Engineering Department of Instituto Superior de Engenharia de Lisboa, C-dots prepared from industrial wastes have been tested, in particular, for the oxidation reaction of primary alcohols.

Thus, the above collaborations, with the Laboratory of Catalysis and Materials of Faculty of Engineering of University of Porto (FEUP), Centro de Química e Bioquímica of Faculty of Sciences of Universidade de Lisboa and Instituto Superior de Engenharia de Lisboa research groups, were fundamental to prepare the materials used in the catalytic applications, being the developed works listed in section 8 of this communication. It must also be mentioned that this interest on the field of transition metal-based catalysts supported at carbon materials gave rise to several M.Sc. and Ph.D. theses and, as a natural consequence, allowed numerous oral and panel presentations in international conferences, namely at *Carbon* and *CarboCat* congresses.

## 2. Oxidation of alkanes

As mentioned above, the immobilization of homogeneous catalysts on carbon supports, thus rendering the systems heterogeneous in order to facilitate the separation and catalyst recycle, to simplify other reaction procedures and/or to increase the stability or the selectivity of the catalyst has been applied to metal C-scorpionate complexes in the field of alkane oxidation [18,19]. As model reaction, the cyclohexane oxidation to cyclohexanol and cyclohexanone (Figure 2), important reagents for the production of adipic acid and caprolactam used for the manufacture of nylon, was chosen.

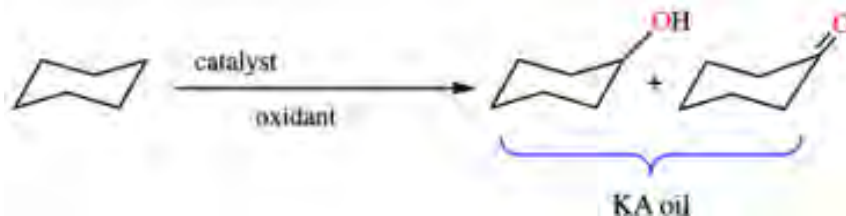


Figure 2. Catalytic oxidation of cyclohexane to cyclohexanol and cyclohexanone.

The iron(II)  $[\text{FeCl}_2\{\kappa^3\text{-HC}(\text{pz})_3\}]$  (pz = pyrazolyl) complex was anchored on three different carbon materials [activated carbon (AC), carbon xerogel (CX) and multi-walled carbon nanotubes (CNT)] in the original form or upon surface treatment (with nitric acid or with nitric acid followed by sodium hydroxide), being the heterogenisation at multi-walled carbon nanotubes treated with nitric acid and sodium hydroxide (CNT-Oxi-Na), the most efficient process. This hybrid material, in particular, led to an outstanding improved catalytic performance of the complex  $[\text{FeCl}_2\{\kappa^3\text{-HC}(\text{pz})_3\}]$  upon heterogenisation (TON up to  $5.6 \times 10^3$  and overall yield of 21% [24]) relative to the homogeneous system.

Simultaneously, interesting results were obtained with the heterogenised C-scorpionate gold(III) catalysts  $[\text{AuCl}\{\kappa^2\text{-RC}(\text{R}'\text{pz})_2\}]\text{Cl}$  (R = H or  $\text{CH}_2\text{OH}$ , R' = H or 3,5-Me<sub>2</sub> pz = pyrazol-1-yl) for the above reaction [25]. Much higher turnover numbers and yield values with lower loading of oxidant were obtained with the hybrid catalysts than with the homogeneous counterparts.

The heterogenised iron(II) and gold(III) systems also offered practical advantages of recycling (by the

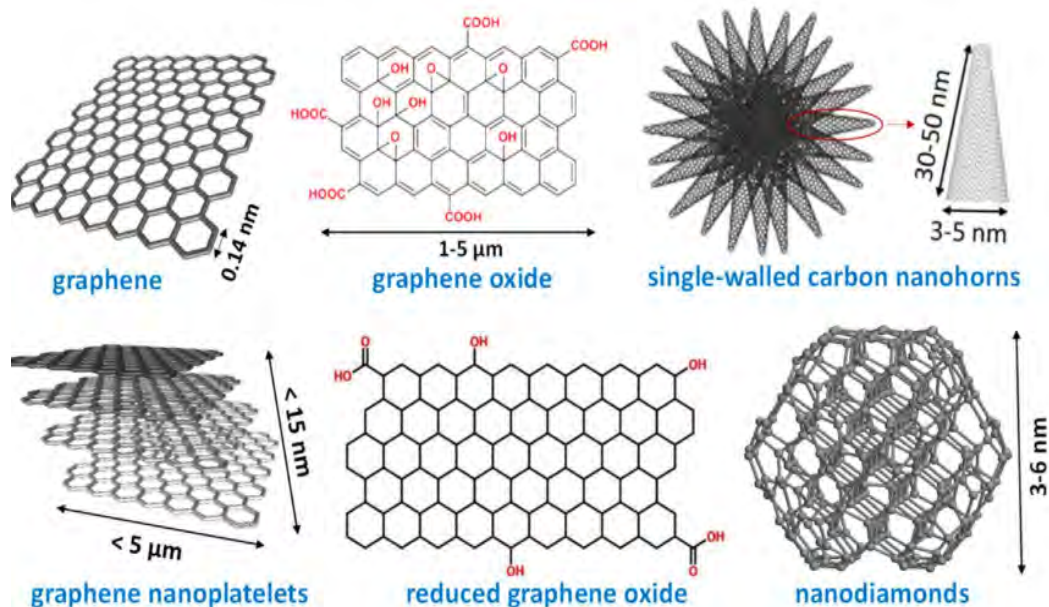
facile separation from products), allowing successive cycles to be performed without significant loss of activity and with a rather high selectivity to the desired cyclohexanol and cyclohexanone mixture. The possibility of applying such complexes as catalyst precursors for the single-pot peroxidative cyclohexane oxidation to cyclohexanol and cyclohexanone, at room temperature, was considered much more attractive and environmentally friendly than the current industrial process.

To note that the hybrid metal complexes-based catalysts showed much higher catalytic activity than gold nanoparticles supported on the same carbon materials [32].

Then, the scope of carbon materials used to anchorage  $[\text{FeCl}_2\{\kappa^3\text{-HC}(\text{pz})_3\}]$  was extended to other nanostructured carbon materials showing a high surface area such as graphene oxide, reduced graphene oxide, graphene nanoplatelets, nanodiamonds and nanohorns (these chosen for the first time as a metal complex support) (Figure 3) [36]. The highly selective heterogenized systems exhibited good activity in producing cyclohexanol and

cyclohexanone with co-catalyst pyrazine carboxylic acid (Hpca) by microwave-promoted oxidation of cyclohexane (yields up to 29%; again, higher values than in homogeneous conditions). Moreover, they were easily recovered and reused for five consecutive cycles maintaining ca. 90% of their initial activity. The oxidized supports (oxidized nanodiamonds,

graphene oxide and oxidized single-walled carbon nanohorns) [36] led to the highest yields of desired oxygenated products, highlighting the importance of the presence of oxygen groups at the materials surface as anchorage sites for the complex  $[\text{FeCl}_2\{\kappa^3\text{-HC}(\text{pz})_3\}]$ .



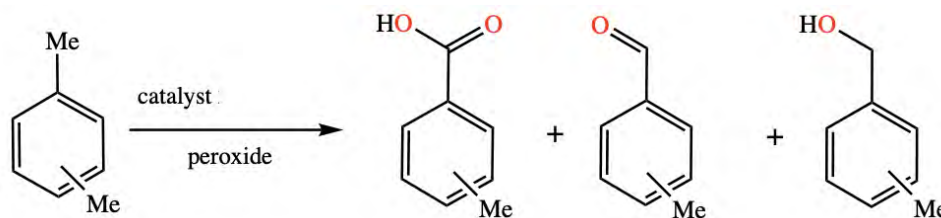
**Figure 3.** Nanostructured carbon materials used as supports. Reproduced with permission of ref. [36] Copyright, 2018, Wiley-VCH.

Recently, the influence of porous carbon supports on the performance of the heterogenized  $[\text{FeCl}_2\{\kappa^3\text{-HC}(\text{pz})_3\}]$  catalyst was investigated [37] using materials with distinct porosity: microporous (GL50-ox, wet oxidized GL50 Norit sample and S, sisal-derived activated carbon prepared by chemical activation) and mesoporous (CMK-3) materials. The heterogenized systems exhibited good activity and rather high selectivity to the formation of cyclohexanol and cyclohexanone mixture from microwave-assisted oxidation of cyclohexane, and allowed their easy

recovery and reuse, at least for four consecutive cycles.

### 3. Oxidation of xylenes

Catalytic oxidation of other hydrocarbons, besides alkanes, was essayed, in particular the oxidation of xylenes (Figure 4), in view of the industrial significance of terephthalic acid production (mainly used in polyethylene terephthalate (PET) manufacturing) from the oxidation of *p*-xylene, and of the limitations of the current Amoco process.



**Figure 4.** Catalytic oxidation of xylene to methylbenzyl alcohol, tolualdehyde and toluic acid.

C-scorpionate vanadium(IV) complexes,  $[\text{VO}_x\text{Cl}_{3-x}\{\kappa^3\text{-RC}(\text{pz})_3\}]$  ( $x = 0$  or  $1$ ,  $\text{R} = \text{SO}_3$ ,  $\text{CH}_2\text{OH}$  or  $\text{CH}_2\text{OSO}_2\text{Me}$ ) [26] heterogenized on oxido-functionalized multiwalled carbon nanotubes (CNT), combined with microwave irradiation, improve the formation of toluic acid: e.g., a *p*-toluic acid yield of 43% (73% selectivity,  $\text{TON} = 1.34 \times 10^3$ ) was achieved using TBHP (70% aq. solution) and a very low loading of  $[\text{VOCl}_2\{\kappa^3\text{-HOCH}_2\text{C}(\text{pz})_3\}]$  ( $3.2 \times 10^{-2}$  mol% vs. substrate) at O-functionalized CNT [26].

The anchorage of the C-homoscorpionate

V-complexes on the CNT is believed to occur by formation of a covalent V-O bond with the CNT surface carboxylate or phenolate groups, displacing a chloride or replacing one pyrazolyl ring of the C-scorpionate, which would behave as a bi-dentate ligand (a well-known feature of these ligands [18,19]). The stability of the supported V-catalysts allowed their reuse with preservation of their activity for six consecutive cycles. After the 6<sup>th</sup> cycle, vanadium leaching is observed, and activity starts to decrease [26].

#### 4. Oxidation of styrene

C-scorpionate Cu(II) complexes such as  $[\text{CuCl}_2\{\kappa^3\text{-RC}(\text{R}'\text{pz})_3\}]$  ( $\text{R} = \text{H}$  or  $\text{CH}_2\text{OH}$ ,  $\text{R}' = \text{H}$  or 3,5- $\text{Me}_2$ ) [30] were immobilized (up to a Cu loading of 2%) on sucrose derived hydrochars, *i.e.*, carbon materials synthesized by hydrothermal carbonization (HTC) of different types of biomass (*e.g.*, glucose, sucrose, fructose or their derivatives, as furfural or hydroxymethyl furfural). The choice (not reported before) of using hydrochars as supports for the

C-scorpionate complexes arose from their easy surface chemistry tuning during the elegant synthetic procedure (HTC) avoiding the usual oxidation (*e.g.*, with  $\text{HNO}_3$ ) treatments. Moreover, the carboxylic groups functionalization obtained by such procedure significantly enhanced the direct immobilization of the C-scorpionate copper(II) complexes, leading to the first recyclable C-scorpionate catalysts used so far for the selective oxidation of styrene to benzaldehyde (Figure 5).

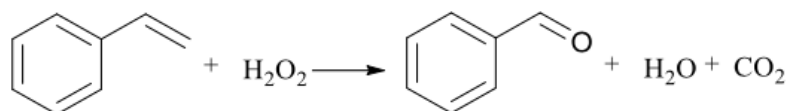
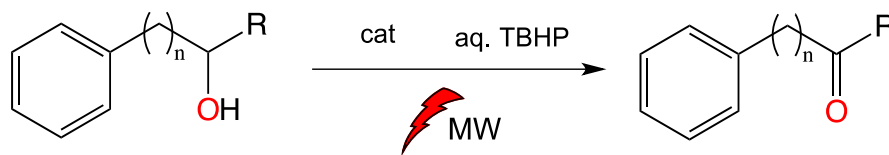


Figure 5. Catalytic selective oxidation of styrene to benzaldehyde.

#### 5. Oxidation of alcohols

In 2016, the highly efficient eco-friendly synthesis of ketones (yields over 99%) from secondary alcohols was achieved by combination of  $[\text{FeCl}_2\{\kappa^3\text{-HC}(\text{pz})_3\}]$  supported on functionalized multi-walled carbon nanotubes and microwave irradiation, in a solvent-free medium [31]. This C-scorpionate iron(II) complex

was the first one of his class to be used as catalyst for the oxidation of alcohols and the developed work led to the award of a WO patent [38]. This catalytic system is currently under scale-up attempts to produce ketones from secondary alcohols using microwave irradiation (Figure 6).



$n = 0$ ,  $\text{R} = \text{Me}$ ;  $n = 1$ ,  $\text{R} = \text{H}$

Figure 6. Catalytic selective oxidation of alcohols to ketones.

More recently [36],  $[\text{FeCl}_2\{\kappa^3\text{-HC}(\text{pz})_3\}]$  immobilized at functionalized nanodiamonds support (used for the first time as supports for iron complexes) was also able to effectively (yields up to 97%) catalyze the MW-induced oxidation of 1- and 2-phenylethanol to acetophenone and 2-phenylacetaldehyde, respectively, and be reused for seven consecutive cycles without losing catalytic activity.

Other types of complexes as oxidovanadium(V) aroylhydrazone complexes derived from (3,5-di-*tert*-butyl-2-hydroxybenzylidene)-2-hydroxybenzohydrazide ( $\text{H}_2\text{L}^1$ ) and (3,5-di-*tert*-butyl-2-hydroxybenzylidene)-2-aminobenzohydrazide ( $\text{H}_2\text{L}^2$ ), *viz.*  $[\text{VOL}^1(\text{OEt})\cdot[\text{VOL}^1(\text{OEt}) (\text{EtOH})]$ ,  $[\text{VOL}^2(\text{OEt})]$ ,  $[\text{Et}_3\text{NH}][\text{VO}_2\text{L}^1]$ ,  $[\text{VO}_2(\text{HL}^2)]\cdot 2\text{EtOH}$ ,  $[(\text{VOL}^1)_2(\mu\text{-O})]$  or  $[(\text{VOL}^2)_2(\mu\text{-O})]$  [28], have also been immobilized on oxidised carbon materials and tested as catalysts for the microwave-assisted solvent-free peroxidative oxidation of 1-phenylethanol to acetophenone by *t*-BuOOH. The immobilization of the above oxidovanadium complexes improved the oxidation efficiency and allowed catalyst reuse preserving their activity.

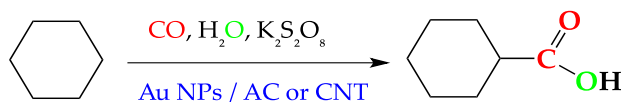
These studies were then extended to the assessment of the catalytic activity of Au nanoparticles deposited on different types of carbon materials, namely, polymer based carbon xerogel, activated carbon,

microdiamonds, nanodiamonds, graphite and silicon carbide by double impregnation and sol immobilisation, which were used as catalysts for the microwave-assisted solvent-free oxidation of 1-phenylethanol, under different conditions [35]. The results showed that the catalytic activity was influenced by several factors, namely, the nature of the support, reaction time and temperature, amount of catalyst, presence of additives, among others. The best values for acetophenone yield (99.9%) were obtained with Au deposited on microdiamonds by the colloidal method. Catalyst recyclability was tested up to six consecutive cycles at the optimized conditions for each catalyst, and it was found that Au on microdiamonds, prepared by the colloidal method, also maintained higher activity after several reaction cycles as compared to the other carbon supports.

#### 6. Carboxylation of alkanes

The carboxylation of  $\text{C}_n$  alkanes to  $\text{C}_{n+1}$  carboxylic acids, using  $\text{CO}$ , is an attractive process for alkane functionalization that might have important applications in industry and surpass the disadvantages of the present synthesis procedures. Therefore, the cyclohexane hydrocarboxylation to cyclohexanecarboxylic acid with  $\text{CO}$ , water and

peroxodisulfate (Figure 7) [33,34], was attempted in the presence of gold nanoparticles deposited by a colloidal method on carbon nanotubes and activated carbon with three different surface chemistries: in their original forms (CNT or AC, respectively), oxidized with  $\text{HNO}_3$  (-ox) or oxidized with  $\text{HNO}_3$  and subsequently treated with NaOH (-ox-Na).



**Figure 7.** Catalytic hydrocarboxylation of cyclohexane.

Au/CNT-ox-Na was the best catalyst, yielding cyclohexanecarboxylic acid up to 88.2% yield, with excellent recyclability (97.5% of the initial activity was maintained after five consecutive catalytic cycles) [33,34].

## 7. Conclusions

In general, the immobilization of the catalysts (in particular C-scorpionate complexes) on functionalized carbon materials revealed to be a good strategy to improve their catalytic activity (remarkable increase of product yields) for alkane, alkene or alcohol oxidations, and to facilitate the catalyst separation and recycling. Moreover, the use of unconventional conditions such as microwave heating proved to be promising toward the promotion of activity, tuning of selectivity, catalyst recycling [19], etc., although remaining virtually unexplored.

## Acknowledgements

The work reported here was supported by the Fundação para a Ciência e a Tecnologia (FCT) through the financial to the Centro de Química Estrutural (UID/QUI/00100/2013-2019), the projects PTDC/EQU-EQU/122025/2010, PTDC/QEQ-ERQ/1648/2014 and PTDC/QEQ-QIN/3967/2014 and the CATSUS PhD Program. CRUP - Ação n.º13/16 is also acknowledged.

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