



Opportunities in the use of carbon materials to develop heterogenized metal complexes for catalytic applications

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ABSTRACT

Carbon materials constitute a broad family of solids that encompass a high variety of physical and chemical properties, including morphology. These materials have shown to be very useful as catalysts supports and, in this context, also for the heterogenization of metal complexes owing catalytic properties. This work is, mainly, the summary of the results obtained in several research projects focused on developing heterogenized molecular catalysts by exploiting the properties of a plethora of carbon materials to address several immobilization procedures.

1. Introduction

A large number of metal complexes, mainly those of organometallic character, exhibit known and relevant uses in the catalysis discipline [1]. They are usually very efficient in soft reaction conditions, being highly active and selective, but highly priced as well. Although the high cost is generally well compensated by the high-added value products synthesized with their aid, the catalytic process would be chemically, economically, and environmentally more favorable if they could be recovered from the reaction media, and eventually reused. Heterogenization of metal complexes can afford the way to recover such valuable but also contaminant compounds. Heterogenization means to confer heterogeneous character to a molecular metal compound that usually acts as a homogeneous catalyst [2], and such a character can be achieved by its immobilization on a solid support. Efendiev et al. [3] refer to immobilized metal complexes as physically heterogeneous and chemically homogeneous catalysts. This means that the anchored species keeps the advantages of a homogeneous catalyst but it is fixed to a macroscopic solid material and thus, it can be easily removed from the liquid phase reaction media by filtration or decantation. However, this description should be nuanced considering that the coordination sphere of the homogeneous complex can be either highly preserved (truly “supported homogeneous catalyst”), or it can be modified by the existence of direct bonds between the metal and the support surface atoms (“heterogeneous molecular catalyst”) [4]. Immobilized metal complexes are also known as hybrid catalysts because they integrate the main characteristics of either, homogeneous and heterogeneous catalysis [5],

or organic and inorganic species [6]. The first one is the concept used for hybrid catalysts in this mini-review.

The advantages of the homogeneous catalysts that should be preserved upon immobilization are: (a) high selectivity, (b) feasible operation under mild conditions, (c) possibility of obtaining reliable information on the active centers, (d) control of catalytic properties by changing composition and, eventually, (e) asymmetric induction. And the main properties of the heterogeneous catalysts that should be attained by developing hybrid catalysts are the facile separation of catalysts from the reaction medium, with the potential capability of reuse, and a higher stability [2,5]. Furthermore, the immobilization brings on the, so called, effect of site isolation [7] that helps to avoid deactivation by the formation of dimers or more complex structures and leads to single site catalysts.

The use of heterogenized homogeneous catalysts bears also some disadvantages, like, for example, the potential leaching of the metal complex during the course of a reaction, or negative effects of the support than can reduce the efficiency of the process, including mass transfer limitations, induction of a certain conformation of the metal complex, and decreased stability of the supported molecule. These drawbacks could be reduced selecting proper immobilization procedures and suitable supports.

The physico-chemical properties of the materials used as supports are decisive for an efficient anchorage of the metal complex in terms of its effectivity in performing the catalytic cycle, and of the stability of the supported species against leaching and against degradation or poisoning. In more detail, some particular aspects of the role of a solid

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material as efficient support for a molecular catalytic species are the following: (a) the location into the pore structure will, likely, involve mass transport limitations that can result in a lower activity, (b) the interaction with the pore walls can affect its molecular conformation, with consequences for the selectivity, and (c) the constraint inside the pores produces the phenomenon known as confinement effect, that has been reported to enhance enantioselectivity, but also chemoselectivity and activity [8–14]. In general, supports must be insoluble in standard organic solvents or water, and mechanically resistant in order to be stable along the many manipulations that are involved in numerous recycling procedures. Among the different materials available for the immobilization of homogeneous catalysts, the most frequently used are materials of inorganic nature such as silica, mesoporous siliceous materials, and zeolites. However, carbon materials play also a pivotal role as catalysts supports [15–22] and this is mainly due the particular outstanding properties that are described next.

Carbon materials are chemically inert in many media, thermally stable (very stable in absence of oxygen) and mechanically resistant, they can be prepared in a wide variety of shapes and morphologies (granules, pellets, extrudates, cloth, fibers, spheres, etc.), and it is relatively easy to recover metal species supported on them. They are very versatile in terms of textural properties and surface chemistry what has shown to be very relevant to modulate and to define the interaction and location of the active species within the support surface. Textural properties include specific surface area, pore volume, pore size distribution, and pores shape. All these aspects can have an influence on the catalyst behavior as they can determine the accessibility and surroundings of the active species and they can have positive or negative effects related with the physical way in which the reactants reach the active site and the products leave it. The positive effects can be related with the previously mentioned confinement effect or to shape selectivity issues, while the negative ones are linked to diffusion limitations. It is convenient to remind that the size of pores of carbon materials ranges from molecular dimensions to holes or fissures related to massive defects, and their shape varies from slit-shaped cracks to cylindrical, conical or irregular forms. Thus, the porosity can be quite regular or it can follow tortuous paths through the solid to form an extensive and non-uniform network. The IUPAC has established the following classification of pores according to their size [23]: micropores (width < 2 nm), mesopores (2 nm < width < 50 nm), and macropores (width > 50 nm). Regarding the effects of the surface chemistry of carbon materials, it should be pointed out that oxygen is one of the most frequent heteroatoms present in them, and that the oxygen surface groups have a major role both, in the anchorage of metal complexes, and in the interaction of the reaction media with the carbon surface. The most common surface oxygen-functional groups include carboxylic acid, carbonyls, phenols, and lactones [24–29]. Other heteroatoms found (or introduced) on the carbon surface for different purposes are: nitrogen, sulfur, phosphorus, and boron. The presence of surface oxygen groups is interesting because they are capable of: (i) increasing the surface polarity and thus its hydrophilicity, (ii) modifying the acid-base properties of the surface, and (iii) creating “anchoring points” that would either favor particular interactions with catalysts or catalysts precursors, or act as reactive sites for the tethering of molecules.

There is a broad variety of carbon materials that have been used so far to prepare carbon-supported catalysts: graphite, carbon black, activated carbon, activated carbon fibers, carbon-covered alumina, graphite intercalation compounds, glassy carbon, pyrolytic carbon, polymer-derived carbon, fullerenes, carbon nanotubes and nanofibers, etc. [18,21]. Among them, activated carbon and carbon black, and in a lesser extent graphite and graphitized materials, have been the most used carbon materials to prepare carbon supported catalysts, both in research studies and in industrial developments [16,21].

This work describes briefly the research work carried out at the department of Inorganic Chemistry of the University of Alicante on the preparation of hybrid catalysts (heterogenized metal complexes) using

carbon materials as support, in a period of time of about 20 years. It is, mainly, the summary of the results obtained in the course of the execution of 5 PhD thesis carried by the following researchers (now doctors): José Antonio Díaz-Auñón, Lived J. Lemus-Yegres, Ion Such-Basáñez, Cristina Constanta Gheorghiu and Mónica Rufete-Beneite; and the collaboration of Dr. María Pérez-Cadenas. This research line had its germ in the combination of the starting of a collaboration with Prof. P.C. L'Argentièrre (from Universidad Nacional del Litoral, Argentina) dealing with the heterogenization of metal complexes, and the experience of the research group of the Alicante University in the preparation, characterization and applications of carbon materials, in particular the knowledge of the use of carbon materials as catalysts supports of Prof. Concepción Salinas Martínez de Lecea and Prof. Maria Carmen Román-Martínez. The first PhD student in this topic, José Antonio Díaz-Auñón, did a very interesting and fruitful research stay in the laboratories of Prof. Howard Alper at the Department of Chemistry in the Centre for Catalysis Research and Innovation of the University of Ottawa. The experience motivated the student and the supervisors to go in depth with this challenging topic that has allowed us exploring many different hybrid catalytic systems. Because of that, and in recognition of the scientific merits of Prof. Alper, it is great honor to participate in the special issue dedicated to him.

The main three variables considered in the research carried out in the frame of the doctoral formation of the mentioned young researchers have been: the type of carbon material used, the metal complex anchored and the general procedure to accomplish the heterogenization of the homogeneous catalyst. In this mini-review, the different attempts to develop useful hybrid catalysts, that had led to very interesting results, have been organized according to the way in which metal complexes have been supported on carbon materials: adsorption, ion-exchange, covalent tethering and supported ionic liquid phase. In each part, the summary of results is, in general, presented chronologically. For a short description of all the carbon materials, properties, and conditions of treatments and reactions mentioned in the text, please see, respectively, tables S1, S2, S3 and S4 in the [supplementary material](#).

2. Immobilization of metal complexes on carbon materials

2.1. Adsorption

The first study carried out in our group in the area of metal complexes heterogenization on carbon materials involved the complex (*trans*-dichloro-bis-tridecylaminepalladium(II), $[\text{PdCl}_2(\text{NH}_2(\text{CH}_2)_{12}\text{CH}_3)_2]$ abbreviated as PdTDA, prepared by the research group of Prof. P.C. L'Argentièrre, and high purity carbon materials, **chars of phenolformaldehyde polymer resin** (named A, A-Na and A2-Na (oxidized A-Na), with surface area ranging from 240 to 610 m^2/g) [30]. The PdTDA complex was deposited by incipient wetness using a toluene solution of the concentration necessary to obtain a catalyst with a 0.3 wt% Pd loading, which was tested in the cyclohexene hydrogenation reaction. The results showed that the carbon supported complex led to catalysts more active and sulfur resistant (tetrahydrofuran (THF) was used as poison) than the homogeneous PdTDA complex and the analogous catalysts prepared with calcined $\gamma\text{-Al}_2\text{O}_3$ as support. The activity of PdTDA/A2-Na was the highest (probably due to higher surface area and richer surface chemistry of the A2-Na support), while catalysts prepared with A and A-Na were only slightly more active than the one prepared with alumina, however the three carbon supported catalysts were noticeably more resistant to poisoning by THF than PdTDA/ Al_2O_3 . It was assumed that poison adsorption on the carbon support prevented the complex deactivation.

Activated carbon has a widespread use in many scientific, industrial and technological areas mainly because of its high performance as adsorbent. The tunable surface area and porosity (achievable by the use of different precursors and activation procedures and conditions) are behind the broad number of applications, being a quite relevant issue in

the use as catalyst support, as they have shown to be useful to modulate and to define the interaction and placement of the active species within the support surface. Considering these interesting properties, activated carbon was also tested as support for the PdTDA complex [31,32]. A series of activated carbons (ACs), including two samples obtained from almond shell (BC-32 and BCaC-30), and several commercial pelletized and granular activated carbons (ROX, RX and GF). Carbon ROX was used in its original form and after some chemical treatments (samples ROX-N, ROX-NT and ROX-SF). The hybrid catalysts, prepared as indicated above, were tested in the hydrogenation of cyclohexene [31] and in the selective hydrogenation of 1-heptyne [32]. The PdTDA/AC catalysts were more active and more resistant to poisoning by THT than both, the homogeneous PdTDA complex and the PdTDA/Al₂O₃ catalyst. The evaluation of the porosity of the carbon supports and heterogenized catalysts, carried out by N₂ adsorption isotherms, allowed to conclude that the PdTDA complex was located in pores smaller than 2 nm, either totally or partially introduced in them or deposited on the pore entrance, in a way in which such pores were blocked. This conclusion was supported by the estimated dimensions of the palladium complex (using the Hyperchem software) that resulted to be (in nm) 4 (long) × 0.6 (high) × 0.3 (wide). Adsorption of this molecule was proposed to occur via Van der Waals interactions of the hydrocarbon chains and basal planes of the carbon materials. This model (Fig. 1) implies that the Pd atom and part of the hydrocarbon chain close to it are not contacting the carbon surface what leaves the electronic structure of Pd unaffected (proposal that was supported by XPS data). The catalytic activity of these hybrid PdTDA/C catalysts in the hydrogenation of cyclohexene was found to increase with the volume of supermicropores (0.7 nm < ϕ < 2 nm) of the carbon supports which was interpreted considering that the PdTDA location in pores of this size, where the reactant concentration around the metal complex is likely higher than in bulk solution, boosts the reaction. Such a situation has been later identified as a confinement effect.

In the case of the 1-heptyne semihydrogenation, the supported catalysts were also more active than the homogeneous complex, and PdTDA/C more active than PdTDA/Al₂O₃; being the catalyst prepared with the activated carbon of narrower porosity the most selective. It was concluded that the location of the PdTDA complex in narrow pores induces shape selectivity, hindering the formation of the alkane.

The positive effect of the porous carbon supports was also set out in similar studies dealing with analogous Rh, Ru and Ni complexes heterogenized by the same procedure [33,34].

Some years later, the immobilization of the PdTDA was carried out on carbon nanotubes [35]. The starting material, named NT, were multiwall carbon nanotubes, prepared using Fe particles as catalysts at the Laboratoire de Chimie de Coordination (CNRS-Université Toulouse) [36] and provided by Prof. Ph. Serp. After a purification treatment with H₂SO₄ to remove metal particles, the NT sample was submitted to the following treatments: ball milling (sample named NTB), oxidation with synthetic air at 773 K (sample named NTOx) and oxidation with HNO₃ solution at room temperature (sample named NTN) (Table S1). Sample NTOx was further purified by treatment with HCl 5 M (sample NTOxD). All these treatments produced the removal of tube caps and many of the remaining Fe particles, and generated some surface oxygen groups. N₂ adsorption data allowed to classify the carbon nanotube samples in two

groups: NT, NTB and NTOx that mainly present on of the tube ends open, and NTOxD and NTN in which a large amount of tubes show both ends open. Thus, the available supports involved different surface chemistry and different proportion of tubular structures with both ends open. The mentioned characteristics showed to have an important impact in the catalytic properties of the hybrid catalysts. Carbon nanotubes with a rich oxygen surface chemistry lead to catalysts with lower catalytic activity, what could be related with unfavorable interactions between the support and the solution (solvent and reactants) that constituted the reaction media. So, in each of the two mentioned groups the samples with the lower amount of surface oxygen groups led to the most active catalyst. However, in the oxidized and/or acid treated supports the proportion of nanotubes with both ends open was higher and this allowed the Pd complex to reach the nanotube cavity (by capillarity phenomena) leading to an enhanced activity attributed to the confinement effect. Thus, the most active catalyst was PdTDA/NTOxD.

The noteworthy adsorptive capacity of carbon materials was also exploited to tether metal complexes with the aid of a specific adsorbate acting as anchor molecule. Several catalytic systems were prepared based on this strategy. The first anchor molecule used was 1-naphtioic acid (Nfa) [37] because of the high affinity of the aromatic rings for the carbon surface, and because it contains a carboxylic acid functionality able to react to form an ester bond with the appropriate functionality of a ligand. The study carried out consisted of analyzing the adsorption and desorption of naphtioic acid on different commercial activated carbon materials (four pelletized carbons (ROX, ROXN, RX3, GF) and a carbon cloth (ACC15)). Adsorption isotherms (at room temperature) using solutions of Nfa in methanol, and Naf desorption, studied in conditions (solvent, temperature, pressure and time) similar to those of the hydrogenation catalytic test, revealed that all the carbon materials tested were able to adsorb and retain amounts of 1-naphtioic acid well above the required quantity to synthesize the desired catalysts. Characterization of the surface area and porosity of the Nfa/C samples (by N₂ and CO₂ adsorption isotherms) allowed to conclude that the Nfa molecule is adsorbed in micropores, what agrees with the molecule dimensions if it adsorbs in a flat configuration (Fig. S1 (supplementary material)).

The idea of the anchor molecule was later developed by researchers of the University of Jaén for the grafting of Pd(II) amino complexes to the surface of a commercial activated carbon (Merck) [38]. The strategy involved the so called Ar-S-F molecules [39], where Ar is an arene moiety that adsorbs on the basal plane of the carbon surface through π - π interactions, F is a chemical function able to bind Pd(II) by complexation, and S is an organic chain that links Ar and F. Ar-S-F molecules were prepared with a nitroso-oxypyrimidinyl residue (Ar) and either *Lys* (Lysine) or *Tren* (tris(2-aminoethyl)amine) accounting for both the S and F components. Palladium was incorporated to the C/Ar-S-F systems from a K₂PdCl₄ solution and the obtained catalysts were used for the hydrogenation of 1-octene. (See scheme in Fig. S2.1-A). The obtained catalysts were very active and selective, what was attributed to the easy accessibility of reactants to the active sites. Small amounts of the S-F-Pd fragments become lixiviated and the reduction of Pd(II) to Pd(0) takes place, leading to stabilized Pd nanoparticles that exhibit a high catalytic activity in the case of the catalyst prepared with *tren* and to a higher agglomeration in the catalyst that contains *lys* giving rise to a steady decrease of catalytic activity.

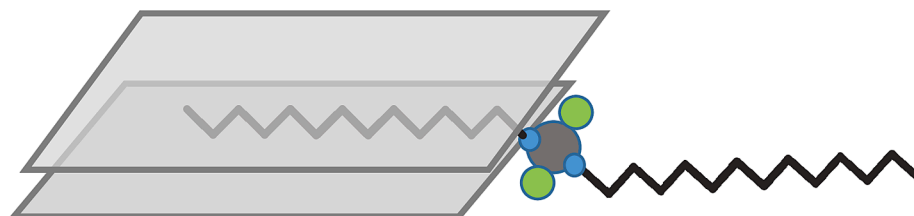


Fig. 1. Model proposed for the immobilization of the PdTDA complex in pores of activated carbon.

Going further in the idea of the anchor molecule, a recent work [40] was carried out with the aim of addressing the challenging issue of the heterogenization of a chiral molecular catalyst, the Rh complex **1,2-bis[(2*R*,5*R*)-2,5-dimethylphospholano]benzene(1,5-cyclooctadiene) rhodium(I) tetrafluoroborate** (abbreviated as (R,R)-RhDuphos) [41]. In this work the selected carbon material was a **high surface area carbon black** that was treated at high temperature to remove surface oxygen groups for reducing the surface polarity (named T2), and the anchor molecule was *L*-Tryptophan (*Trp*). Catalysts with different amount of supported *Trp* were prepared, and it was found that *Trp* was effectively adsorbed on the carbon surface, being an excess of adsorbed tryptophan respect to the desired molar Rh loading (a *Trp*/Rh molar ratio of 8) necessary to assure the catalysts stability (to hinder the Rh complex leaching). (See scheme in Fig. S2.1-B). Characterization by XPS revealed that Rh interacts with O and/or N what allowed to assume that the coordination with the anchor molecule was established. The obtained heterogenized catalysts were tested in the asymmetric hydrogenation of 2-methylacetamidoacrylate (MAA), showing that they were very active, keeping an acceptable enantioselectivity, and they showed to be reusable.

The RhDuphos complex was also directly immobilized by means of π - π interactions of the ligand aromatic ring with the surface of demineralized commercial **carbon nanotubes** (sample CD) [42]. A schematic picture of this interaction can be seen in Fig. 2. The procedure to incorporate the Rh complex in the carbon support is described in Table S3 (#1). In order to promote the mentioned anchorage, sample CD was heat treated (He flow, 10 K/min up to 1173 K) to remove surface oxygen complexes as much as possible in order to produce a non-polar support surface (CDtt). TEM analysis of the hybrid CDtt-RhDuphos catalyst revealed the presence of some small metal particles (average size is 2 nm), what was in agreement with the presence of Rh(0) determined by XPS. This information indicated that the CDtt support promoted the reduction of the Rh complex. Although catalyst CDtt-RhDuphos was very active producing a high substrate conversion, it showed a very poor enantioselectivity. Likely, the presence of metallic Rh and the interaction of the aromatic ring of the complex with the support surface are important modifications of the complex structure that make it noticeably less enantioselective.

2.2. Ion exchange

The presence of ionizable oxygen groups on the carbon materials surface can be exploited to immobilize metal complexes by an ion exchange process. In this regard, the chloride ligand in complex **[Rh(μ -Cl)(COD)]₂** (abbreviated as RhCOD) was planned to be substituted by carboxylate groups present on the surface of a **pelletized activated**

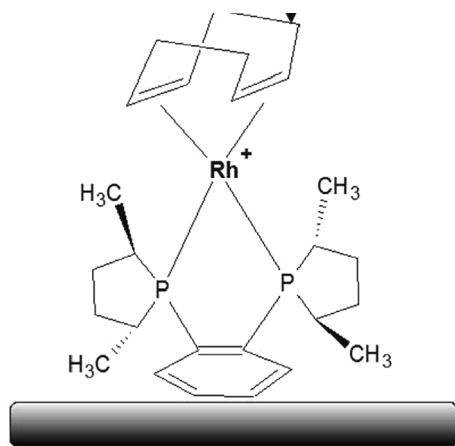


Fig. 2. Schematic plot of the interaction of RhDuphos on the surface of sample CDtt.

carbon [43]. The selected support was the ROX activated carbon that was used both, pristine and after having been oxidized by treatment with a solution of HNO₃ (sample ROX-N). The heterogenization process was carried out by mixing the support with a methanol solution of the metal complex (Table S3 (#2)). The expected ion exchange process involved the release of HCl with the subsequent modification of the ionic conductivity of the solution, which was used to quantify the complex exchange. The obtained results showed that the extent of such ion exchange in the oxidized carbon was higher than in the original one (about 10 times higher, 64% vs 7%). As both catalysts contain the desired 1 wt % Rh, it was stated that in the original carbon, the complex was mainly retained by adsorption while it was mainly ion exchanged in the oxidized one. The catalysts were tested in the **hydroformylation of 1-octene** showing the two of them conversion levels similar or higher than that of the homogeneous complex, but yielding products with a higher *n*/*i* ratio. Interestingly, the sample prepared with the oxidized support, in which the Rh complex was immobilized by electrostatic interactions, exhibited a higher stability against lixiviation and could be used in successive catalytic runs.

The chiral RhDuphos complex was also immobilized on carbon materials making use the support surface oxygen groups and the cationic nature of the metal complex **[(Rh((R,R)-Me-Duphos)(COD)]BF₄** [42]. The study was carried out using **carbon nanotubes and carbon xerogels**. The commercial carbon nanotubes samples C and C_{OH} were treated as follows: C was demineralized and oxidized with ammonium persulfate solution (sample CDS), and C_{OH} was demineralized and functionalized in a way in which butanoic acid was grafted to the carbon surface by means of siloxane type bonds, to act as a linker species connecting the support surface and the metal complex (C_{OH}DL). The carbon xerogel samples used were CX1, CX2 (of different porous structure) and CX2S (oxidized with ammonium persulfate solution). The procedure used to immobilize the RhDuphos complex in the mentioned carbon materials is described in Table S3 (#1). (See scheme in Fig. S2.1-C). The obtained results showed that the Rh loading did not reach the nominal one (around 0.6 wt% vs 1.7 wt%). In the case of supports CDS, CX1, CX2 and CX2S, this pointed to a limited accessibility or capability of the surface groups to interact with the cationic Rh complex, but in the case of support C_{OH}DL the amount of Rh loaded was the expected one considering the amount of L tethered. According to XPS data, the Rh species were more homogeneously distributed in carbon nanotubes than in carbon xerogels in which the active sites are more externally located, and TEM images showed that no metallic particles were formed. The hybrid catalysts were tested in the asymmetric hydrogenation of 2-methylacetamidoacrylate (MAA) (Table S4(#5)). The obtained hybrid catalysts are active and enantioselective, although their catalytic performance was not as good as that of the homogeneous RhDuphos complex, probably due to the modifications of the Rh coordination sphere by the anchoring process and to diffusion limitations. Leaching constitutes an important drawback of hybrid catalysts, but it was found that the presence of surface carboxylic groups hinders it to some extent. The catalyst prepared with support CX2S showed an interesting behavior as it was active and enantioselective in long term experiments, and it was recyclable, as well.

2.3. Covalent tethering

Frequently, the oxygen surface groups of carbon materials have been used for the creation of covalent bonds with appropriated functionalities of the coordinated ligands of the metal complex. The most versatile and used oxygen surface groups are those resembling carboxylic and phenol functionalities. The common procedure to exploit carboxylic groups involves their transformation into acyl chloride functionalities (1, in Fig. 3) what can be done by treatment with thionyl chloride (Table S3 (#4)). This facilitates the reaction with ligand functionalities, like amine or alcohol, to create covalent bonds, amide- or ester- type. This methodology was used to tether the diphosphine ligand named HONP (2 in

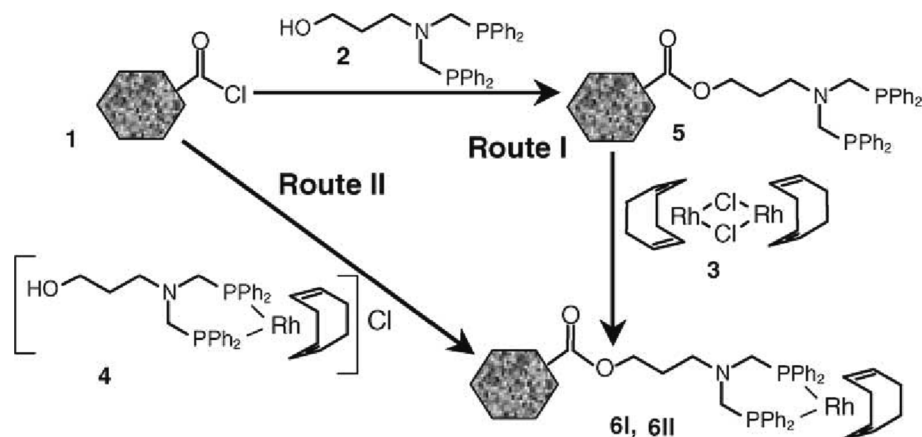


Fig. 3. Schematic picture of the two synthetic routes leading to Rh(COD)/GF-ONP hybrid catalyst.

Fig. 3), to an **activated carbon** that was previously oxidized by treatment with HNO_3 solution (sample GFN). The HONP ligand was tethered either as independent molecule, or after having been coordinate to the Rh(COD) complex (3 in Fig. 3) to form the “anchorable” Rh complex (4 in Fig. 3) [44]. These two alternative synthetic ways are depicted in Fig. 3.

The XPS analysis allowed to confirm that the steps for the catalysts’ preparation were successfully performed, and the formation of Rh-P bonds was identified, leading to assume that the desired Rh complex was obtained. Solid state ^{31}P NMR analysis revealed the partial oxidation of phosphines in catalyst Rh(COD)/GF-ONP (6I), while phosphines remained unchanged in Rh(COD)/GF-ONP (6II), allowing to conclude that route II was more efficient for RhCOD heterogenization because the HONP ligand is stabilized by the previous coordination to Rh. The hybrid catalysts prepared in this way were active and selective in the hydroformylation of 1-octene (Table S4 (#3)). The catalyst prepared by route II presented an interesting catalytic behavior, as they showed to be very active and selective to the linear aldehyde, keeping these properties in four consecutive catalytic runs.

Surface hydroxyl groups present on inorganic materials and polymers have been frequently used to immobilize metal complexes by reaction with a trialkoxysilane functionality present in a ligand, what allows to create a siloxane bond [45,46]. This strategy was used [47] for the heterogenization of $[\text{Rh}(\text{COD})(\text{NH}_2(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3)]\text{BF}_4$ (COD = cyclooctadiene), abbreviated as Rh(NN)Si, in two **commercial microporous activated carbons** (GF and ROX) and **multiwall carbon nanotubes** (NT). The Rh(NN)Si complex was synthesized starting from the commercial $[\text{RhCl}(\text{COD})]_2$ following the procedure reported in the literature [48]. Hydroxyl functionalities can be relatively easily developed on the surface of carbon materials by oxidation using synthetic air [49] (samples GFOx, ROXOx and NTOx). To the best of our knowledge this was the first study in which phenol type groups were exploited to immobilize metal complexes on the surface of carbon materials by the creation of siloxane bonds. The procedure for the immobilization of Rh(NN)Si (2 wt% Rh loading) is described in Table S3 (#5). The hybrid catalysts prepared in this way were used for the hydrogenation of cyclohexene (Table S4 (#1)) showing that the immobilized Rh(NN)Si complex was noticeably more active than the homogeneous one. This was proposed to be due to positive electronic modifications suffered by the Rh complex upon anchoring, and also by the confinement effect caused by the support porosity (the Rh(NN)Si dimensions allowed its location in supermicropores or narrower mesopores). The most active of the hybrid catalysts tested was the one prepared with the NT support, and this led to consider that the Rh complex was, at least partially, located in the hollow cavity of the carbon nanotubes. All the hybrid catalysts tested were recyclable with an increase of the catalytic activity in the second and following runs. Thus, the study carried out revealed

the effective anchorage of the Rh(NN)Si complex on the surface of the carbon materials and also the occurrence of some modifications under reaction conditions leading to more active species.

The desired $-\text{OH}$ phenol groups can be created also by treatments with aqueous solutions of oxidizing agents like nitric acid, ammonium persulfate and hydrogen peroxide, able to produce them in a larger extent, although less selectively [50]. With the purpose of determining the effectivity of these liquid phase oxidation treatments, the previously commented study was extended [51], focused on the **activated carbon** ROX and the derived samples ROXNb and ROXS. (See scheme in Fig. S2.1-D). The N_2 adsorption isotherms showed that the textural properties of the activated carbon were only slightly modified by the oxidation treatments and, thus, the effect of the surface chemistry was analyzed without implications of the textural properties. The liquid phase treatments generate a high amount of phenol type functional groups but other oxygen functionalities are also extensively created. The presence of a large amount of oxygen surface complexes can hinder the accessibility of the metal complex to the effective anchorage sites (the $-\text{OH}$ phenol type groups). Also, if they are located in narrow pores, the anchorage process can be impeded. Regarding the effect of the surface chemistry, it was found that the Rh(NN)Si complex was more externally located in the ROXNb and ROXS supports than in ROX and ROXOx. Difficulties for the metal complex to reach an inner efficient position could be due the blockage of the pores entrance by a large amount of surface oxygen groups. The hybrid catalyst prepared with ROXOx (oxidized with air) was the most active, being also stable and reusable, with negligible leaching, what allowed to conclude that an extensive oxidation of the support surface had a negative effect on the catalytic activity.

Once decided that oxidation with air was the most suitable way to develop phenol type surface groups, a wider series of carbon materials was tested as support for the Rh(NN)Si complex [52]. Such a study allowed to deepen into the knowledge of the effect of porosity on the location of the rhodium complex in the support surface. The mentioned series of carbon materials included: a commercial pelletized **activated carbon** (ROX); **carbon fibers** synthesized from coal tar pitch (A20); a commercial **activated carbon cloth** (ACC); **multiwalled carbon nanotubes** (NT), and **carbon nanofibers** (GANF) prepared by CVD (Chemical Vapor Deposition) [53], which were oxidized by treatment with synthetic air. It was determined that the surface concentration of phenol type groups was higher in samples NTOx and GANFOx, and this was considered interesting because three $-\text{OH}$ groups in close proximity are necessary for the effective anchorage of the Rh(NN)Si. XAFS analysis revealed that the coordination of Rh in the heterogenized complex remained as in the original molecule, and XPS data revealed that in all cases, except in the catalyst prepared with NTOx, the Rh/N atomic ratio was the corresponding to the Rh(NN)Si complex. Rh and N signals were

not observed in the hybrid catalyst prepared with the NTOx support and since the analysis depth of this technique is about 2 nm, this finding led to conclude that the complex was located inside the tubular cavity (schematic drawing in Fig. 4). The heterogenized catalysts prepared were tested in the hydrogenation of cyclohexene, and with the exception of the one prepared with A20Ox, they were more active than the homogeneous complex. Among them, the catalyst prepared with support NTOxD was significantly the most active (TOF 50 times higher than for the homogeneous Rh(NN)Si complex, and about twice than for the catalyst prepared with GANFOx, the second most active). The reuse tests showed that, with the exception of the catalyst prepared with A20Ox that remained inactive, the catalytic activity of all the hybrid catalysts increased in a second catalytic run and it was maintained in three more consecutive catalytic runs. Some Rh leaching was observed only in the catalysts prepared with ACCOx and A20Ox. The most active catalysts for cyclohexene hydrogenation, NTOxD-Rh and GANFOx-Rh, and sample ROXOx-Rh, for comparative purposes, were tested as well in the hydrogenation of carvone (this substrate is a terpenic monocyclic ketone containing three different functional groups that can be hydrogenated: a carbonyl (C=O) and two carbon-carbon double bonds (C=C, endocyclic and exocyclic) (Table S4 (#4) for reaction conditions). Complete conversion of carvone was achieved in about 15 and 40 min with catalysts NTOxD-Rh and GANFOx-Rh, respectively, while catalyst ROXOx-Rh was much less active. These three catalysts were stable and recyclable. The catalyst prepared with carbon nanotubes was selective to the saturated ketone (carvomenthone), while the one based on the carbon nanofibers was very selective to the unsaturated ketone (carvotanacetone). These differences in selectivity were considered to be related with differences in the dimensions of the tubular cavities. In summary, the reaction was faster using catalyst NTOxD-Rh, but selectivity was higher in the case of GANFOx-Rh.

The obtained results showed that, in general, the appropriate support should have high surface area with pores broader than narrow micropores. The average pore diameter must fit the compromise of being small enough for the confinement of the metal complex to occur, but sufficiently large to assure the accessibility of the reactants to the active sites. Also, it has been found that the tubular structure with two ends opened (present in catalysts NTOxD-Rh and GANFOx-Rh) leads to the best catalytic results. The most suitable geometrical properties depend on the volume of the substrate to be hydrogenated, and thus, in the case of carvone hydrogenation the active species must be located in pores of several nanometers, like those present in NTOxD and GANFOx.

Trying to be more accurate to define the suitable size of the tubular cavity, the next work on the topic was focused on the use of four carbon nanotubes samples of different inner diameters as support for the heterogenization of the Rh complex Rh(NN)Si [54]. These carbon nanotubes samples, obtained from different sources, were named NT4, NT5,

NT7 and NT10, where the cipher stands for the average diameter of the tubular cavity of each one. The samples were submitted to chemical treatments to remove the residues of the metal catalysts used for their synthesis, and they were oxidized by heat treatment with synthetic air. The carbon nanotubes samples were characterized by TEM, Raman spectroscopy, N₂ adsorption and TPD. The amount of Rh loaded varied from 0.20 to 0.44 wt% and analysis of this information allowed to determine the extent in which phenol type groups were used to anchor the complex. In the narrower carbon nanotubes (NT4) only about 50% of the -OH groups seemed to be accessible for the Rh(NN)Si immobilization, while for the NT5 and NT7 samples, it was about 90%. The four hybrid catalysts were tested in the hydrogenation of cyclohexene and in the hydrogenation of carvone, and they showed quite different catalytic activity. For both reactions, the order in catalytic activity (regarding the support used) was NT4-Rh < NT10-Rh < NT5-Rh << NT7-Rh, suggesting a clear effect of the diameter of the nanotubes inner cavity to enhance the catalytic activity. The characterization and catalytic activity results allowed to state that the Rh complex was not accommodated inside the tubular cavity of the thinner carbon nanotubes (NT4) and that leaching was quite high in sample NT10-Rh (about 55% in front of <7% in the rest of samples). In general, it was concluded that the nanotube inner diameter strongly influences the location of the complex in the support and also the stability of the heterogenized complex. If the complex is located inside the tubular cavity, the diameter of such cavity also regulates the effect of the constrained environment. (See scheme in Fig. S2.2-A).

With the aim of further exploring the role of the porosity of carbon materials to develop effective hybrid catalysts, and as a result of comments and discussions with researchers expert in other types of carbon materials, the study was focused on analyzing the performance of carbon xerogels and carbon nanofibers [55,56] as supports for Rh(NN)Si. Two mainly mesoporous carbon xerogels, CX1 and CX2 of different maximum pore diameter, 26 and 10 nm, respectively, and carbon nanofibers obtained from lignin (NFL) which are essentially microporous and with a considerable external surface area, were used as supports. They were oxidized by thermal treatment with synthetic air to create the necessary surface phenol type groups (see Table S2). The textural and morphological characterization showed that the structure of the carbon xerogels can be described by an interconnected pore network with pores ranging in size from meso- to micropore. The NFL nanofibers are massive (without an internal hole), their mean individual diameter ranges between 50 and 100 nm, and they contain mainly micropores, although the nanofibers entanglement leaves also voids of several nanometers. XPS characterization of the hybrid catalysts revealed that the electronic state of Rh is preserved upon heterogenization and that the location of Rh atoms is more internal in catalyst NFLOx-Rh, followed by catalysts CX1Ox-Rh and CX2Ox-Rh. It was found that the anchored Rh complex produces the partial blockage of the microporosity, because it is located either at the entrance of some micropores, or partially or totally inside them. These hybrid catalysts shown to be more active than the homogeneous Rh(NN)Si complex for cyclohexene hydrogenation. Catalysts CX1Ox-Rh and CX2Ox-Rh behave similarly, and an induction time for the reaction starting was observed. Catalyst NFLOx-Rh was found to be the most active, suggesting that the confinement effect is more pronounced when the Rh complex is more internally located. For carvone hydrogenation, the CX2Ox-Rh catalyst is more active and more selective to carvotanacetone, likely because the more external location facilitates the transformation of this relatively voluminous substrate and it exerts also shape selectivity. However, these catalysts are not as active as those prepared with the carbon nanotubes (NT (or NT7)) and the hollow carbon nanofibers (GANF), previously commented. The catalytic activity of the xerogel based catalyst was enhanced (and the induction period is absent) in consecutive catalytic runs, while it decreased for the NFLOx-Rh catalyst. TEM analysis revealed the presence of Rh nanoparticles in the used catalysts and they were noticeably larger in the case of catalyst NFLOx-Rh. These results

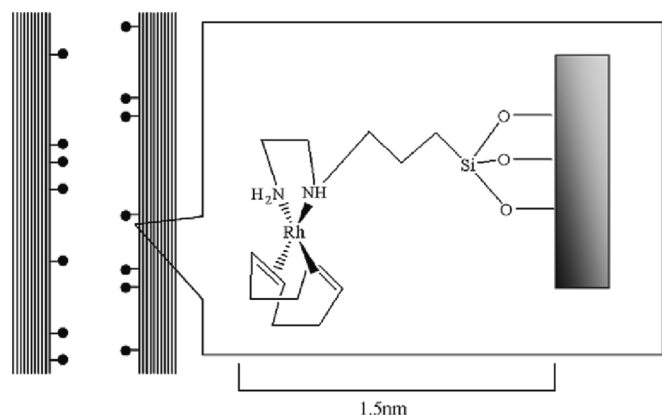


Fig. 4. Schematic drawing of the location of the Rh(NN)Si complex in the carbon nanotube inner cavity.

showed that nature of the support has a strong effect in the stability of the anchored Rh complex.

Although carbon nanotubes and carbon nanofibers demonstrated to be efficient supports for the immobilization of metal complexes, they bear technical drawbacks associated to their powdery nature. Their handling in catalytic processes becomes troublesome as filtration problems in slurry phase operation, and pressure drop in gas phase operation, occur. These inconveniences could be prevented if the carbon filaments would be incorporated into larger objects like, for example, a ceramic monolith [57]. On the other hand, carbon xerogels, for which the synthesis procedures allow to tune the size and volume of *meso*- and *macropores* [58], can be prepared in granular form (by grinding the synthesized material) of suitable size for easy manipulation. Thus, the Rh(NN)Si catalyst was immobilized on a **ceramic monolith covered with carbon nanofibers** (M–CNFOx) and on a broad pore **carbon xerogel** (CX3Ox) [59] (See scheme in Fig. S2.2-B). Both carbon supports were oxidized with air. CNFOx displayed a fishbone structure while CX3Ox looked spongy like, showing a tortuous pore network. The maximum/ average pore size (in nm) of these materials were, respectively, 80/23 and 40/20. The main purpose of the study was to take advantage of both their open porous structure, which should decrease mass transfer limitations, and their morphology, which was expected to facilitate the catalyst handling and to avoid difficult separation processes. As in previous works, the hybrid catalysts were more efficient for cyclohexene conversion than the Rh(NN)Si complex used in homogeneous phase and they were stable against leaching. Kinetics of the cyclohexene hydrogenation was monitored by measuring H₂ consumption and, although M–CNFOx–Rh was more active in the first 30 min, after about 1 h, both heterogenized catalysts gave similar cyclohexene conversion values. After use, the Rh complex appeared partially reduced in the form of nanometer-sized Rh particles, and in this state, the catalyst showed a higher catalytic activity. The M–CNFOx–Rh catalyst was interesting due to advantages like easy handling, immediate recovery from the reaction media, and good mechanical strength.

Once convinced of the benefits and possibilities of the confinement of metal complexes in suitable cavities like those characteristic of the carbon nanotubes, new carbon based hybrid catalysts were developed by the immobilization of known and effective metal complexes [60]. The target was the famous Wilkinson's catalyst [RhCl(PPh₃)₃] [61] and the objective was to attain the covalent anchorage of the Wilkinson's catalyst (more precisely a derivative of it), in a way in which its environment resembles that of the homogeneous phase. The synthetic design for that included the following issues [60]: a) the anchorage to the support was created through an ester type covalent bond formed by reaction between surface carboxylic type groups and an alcohol functionality of a ligand, b) such a ligand was a linear organic molecule (6-amino-1-hexanol), that should keep the complex apart of the support surface, c) the amino donor group substituted a phosphine ligand of the original Wilkinson's catalyst, and d) the carbon materials used were an **activated carbon** (ROX) and **carbon nanotubes** (NT).

The foreseen anchorage is schematically depicted in Fig. 5. (See also scheme in Fig. S2.2-C).

Carboxylic groups were created by oxidation with (NH₄)₂S₂O₈ solution and they were later transformed into acyl chloride groups (treatment with SOCl₂ solution, Table S3(#4)). The metal complex anchorage process comprises the following two steps: (i) reaction of the –OH end the 6-amino-hexanol (having been the amino group previously protected) with the surface acyl chloride groups, and (ii) substitution of a phosphine ligand of the Wilkinson's catalyst by the anchored amine (Table S3 #6–9#). The prepared hybrid catalysts were named ROXAA-RhW and NTAA-RhW. Both contain about 0.5 wt% Rh, and N₂ adsorption and XPS measurements allowed to state the Rh complex location in mesopores of the activated carbon, and partially placed inside the carbon nanotubes. The catalysts were tested in the hydrogenation of cyclohexene (Table S4(#1)), and it was found that the activity of ROXAA-RhW was close to that of the homogeneous Wilkinson's catalyst,

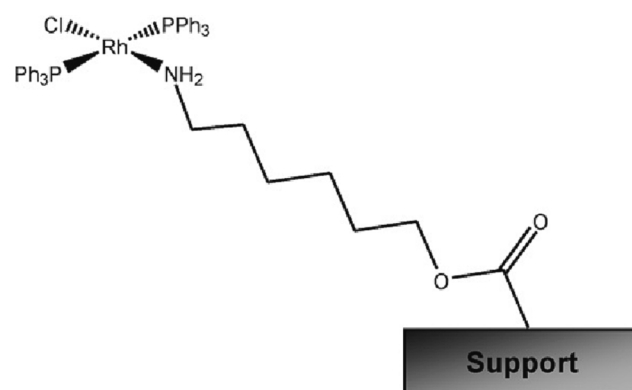


Fig. 5. Scheme of the covalent heterogenization of a derivative of the Wilkinson's catalyst.

while NTAA-RhW showed a noticeably higher activity. This result was found to be very interesting, in particular because the Rh complex contains an amine instead of a phosphine ligand. The hybrid catalysts obtained shown to be reusable if any the following procedures were followed: i) PPh₃ was added to the reactor before the catalyst recovery by filtration in air (to preserve the Rh coordination sphere) or ii) spent reaction solution is removed avoiding the exposure of the catalyst to air.

Collaboration with the research group of prof. Ph. Serp from Laboratoire de Chimie de Coordination, Composante ENSIACET and Université de Toulouse, UPS, INPT was the point to develop a covalent anchorage of Rh chiral complexes on **carbon nanotubes** for enantioselective hydrogenation reactions [62]. At the time of the study (2014), it was probably the first work focused on such a system. Immobilization of the Rh complex was accomplished through an amide bond created between the oxidized carbon material and amino tagged ligands. Pyrrolidine-based diphosphine ligands (PPM, 2S,4S-4-diphenylphosphino-2-diphenylphosphinomethylpyrrolidine) were selected as they are efficient ligands in rhodium(I) catalyst used for the asymmetric hydrogenation of olefins [63]. The carbon nanotubes named CNT in this study were purified (demineralized) by treatment with acids, oxidized by treatment with nitric acid solution, and treated with SOCl₂ to transform the carboxylic acid into acyl chloride groups (Table S3 (#4)). Two chiral diphosphines were synthesized [62] (N-(*tert*-butoxycarbonyl)-(2S,4S)-4-diphenylphosphino-2-[(diphenylphosphino)methyl]-pyrrolidine, (S,S) (named 1a) and N-(*tert*-butoxycarbonyl)-(2S,4S)-4-[2',5'-diphenylphosphinyl]-2-[(2',5'-diphenyl-phosphinyl)methyl]-pyrrolidine, (S,S) (named 1b)). The procedure for the anchorage of the chiral phosphines to the functionalized carbon nanotubes and the incorporation of the Rh complex are briefly described in Table S3 #10 and #11, respectively.

The hybrid catalysts (see scheme in Fig. S2.2-D) were tested in the asymmetric hydrogenation of two different substrates: methyl 2-acetamidoacrylate and α -acetamidocinnamic acid (identified as 2a and 2b, respectively). To evaluate the stability of the hybrid catalysts under reaction conditions a run (24 h) was carried out in absence of substrate, and no leaching was detected. The hybrid catalysts CNT1a-b-Rh were active but their enantioselectivity for the hydrogenation of substrate 2a was moderate. Interestingly, the hybrid catalysts kept a high catalytic activity after 3 consecutive cycles, preserving their enantioselectivity. In the case of the hydrogenation of α -acetamidocinnamic acid, the hybrid catalysts CNT1a-b-Rh were able to yield good substrate conversions (71–75%) with enantiomeric excess in the range of 54–63%. These were considered very encouraging results. In comparison with reported homogeneous catalytic systems, CNT1a-b-Rh shown to be slightly less active but clearly more enantioselective. The study of the spent catalysts revealed that leaching was low, some alteration of the complex structure happened and some quite small Rh nanoparticles were detected that must be stabilized by the chiral ligands, keeping thus the

enantioselectivity.

2.4. SILP

SILP (Supported Ionic Liquid Phase) catalysts can be also considered as a suitable alternative for the development of immobilized homogeneous catalysts. In this methodology, the molecular homogeneous catalyst dissolved in ionic liquid (IL) is deposited on a solid material [64]. Fig. 6 shows a scheme of this kind of supported catalysts. As it is known, ionic liquids are organic salts, liquid at room temperature, that have very good capabilities as solvents [65] and, mainly because of that, they have very interesting applications in catalysis [66]. In SILP state, the active species does not suffer important modifications of its chemical and physical properties, being the chemical and conformational characteristics preserved. Compared to analogous biphasic systems, the SILP catalysts offer a larger interphase for the catalytic process to occur. As the IL solution is either adsorbed on the support surface or fills the porosity, the textural and chemical surface properties of the solid material largely affect the catalyst-support interaction and also the interfacial interaction of the supported solution with the reaction media. As a consequence, the support properties have a high influence in the performance of the SILP catalysts.

As carbon materials are very suitable as catalysts supports, they can be also used in SILP systems. Thus, our research line on the heterogenization of metal complexes for catalytic applications, included also an insight on the immobilization of ionic liquids on porous carbons [67]. The carbon materials tested were two **spherical activated carbons** (GeA and KA), a **carbon black** (T), a **commercial activated carbon** (SA), an **activated carbon produced from agricultural waste** (BPS) and **carbon nanotubes** (C_{OH}), and the selected ionic liquid (IL) was [bmim][PF₆] (1-butyl-3-methyl-imidazolium hexafluorophosphate). The mentioned carbon materials were oxidized by different procedures to study not only the effect of the textural properties but also the effect of the surface chemistry in the IL loading. The obtained results can be summarized as follows: The total pore volume of the supports determined the maximum amount of IL that could be loaded (with relatively low effect of the porous structure or the oxygen surface chemistry). The supported IL fills the pores, but leaves some blocked porosity, so the picture does not correspond to a supported film. IL leaching in water under general hydrogenation conditions was, in general, quite low but it was found to increase with the amount of IL loaded and with the surface oxidation.

With the knowledge acquired in that study, SILP catalysts were prepared with carbons GeA, KA, T and SA, the [bmim][PF₆] ionic liquid, and the [RhCOD] complex (chloro(1,5-cyclooctadiene)rhodium(I)

dimer) [68]. (See scheme in Fig. S2.3-A). The IL and Rh loading were 20 wt% and 1 wt%, respectively, and the prepared catalysts were tested in the cyclohexene hydrogenation in toluene. Reference tests in homogeneous phase showed that the catalytic activity was higher than in analogous measurements done in biphasic systems, suggesting that the IL surrounding the complex hindered the access of reactants to the active center. However, all hybrid SILP catalysts were more active than the biphasic system, and their catalytic behavior was influenced by the support properties. The catalyst prepared with the activated carbon SA was even more active than the homogeneous system. Rh leaching was very low in all cases, generally lower than 1%, and it was concluded that the ionic liquid helped to stabilize the catalyst. Some Rh aggregates were detected by TEM in used catalysts, and, although their structure and composition were not well determined, XPS analysis allowed to rule out the presence of Rh(0). The carbon based SIPL catalysts prepared kept their conversion in three consecutive catalytic runs and thus, they resulted to be reusable.

The SILP methodology was also used to heterogenize the chiral RhDuphos catalyst on carbon materials [69] with the ambitious purpose of preserving the steric configuration of the Rh complex. The carbon materials selected for this study were the two **spherical activated carbons** named GeA and KA, the **carbon black** named T, and the **commercial activated carbon** known as SA, and the ionic liquid (IL) used was [bmim][PF₆] (1-butyl-3-methyl-imidazolium hexafluorophosphate). (See scheme in Fig. S2.3-B). The SILP catalysts, prepared with IL loadings of 20 and 40 wt%, were tested in the asymmetric hydrogenation of 2-methyl-acetamidoacrylate (MAA), using water as solvent, in catalytic tests of 1.5, 3 and 21 h. Homogeneous phase and biphasic reference tests were also performed showing that the biphasic system was clearly less enantioselective than the homogeneous one. All SILP catalysts with 20 wt% IL loading gave a high MAA conversion, and comparison with biphasic and homogeneous systems (at 3 h) showed that they were as active as the biphasic system, although less active than the homogeneous one. MAA conversion was close to 80% in 1.5 h tests and above 94% in 3 h tests for all the prepared catalysts, but enantioselectivity was low. The catalyst prepared with the carbon black, support T, gave the highest conversion (99%) and enantioselectivity (21%), very close to that obtained with the biphasic system (27%). However, and very interesting, when the catalysts were prepared with a 40 wt% IL, the enantioselectivity increased for all catalysts, being 71% for the one prepared with the carbon black material. This catalyst was tested in successive runs and was found to be reusable. This study allowed to conclude that using the appropriate carbon support and IL loading, hybrid SILP chiral catalysts with acceptable enantioselectivity and reusability can be prepared.

3. Conclusion

The broad family of carbon materials offers numerous opportunities to find the right solid able to be used as support for the heterogenization of metal complexes. The tunable porosity can stabilize species and provide the confinement effect. The modifiable surface chemistry affords many options to design covalent and non-covalent interactions with the support surface. The multiple morphology options provide possibilities for reactor design and catalyst handling.

4. Author statement

As the only author of the minireview manuscript I have been responsible of the manuscript conception, organization, writing and revision. The presented data were obtained by junior researchers under my supervision, thus I also participated in the design of the experimental work, data interpretation and elaboration of the corresponding published papers.

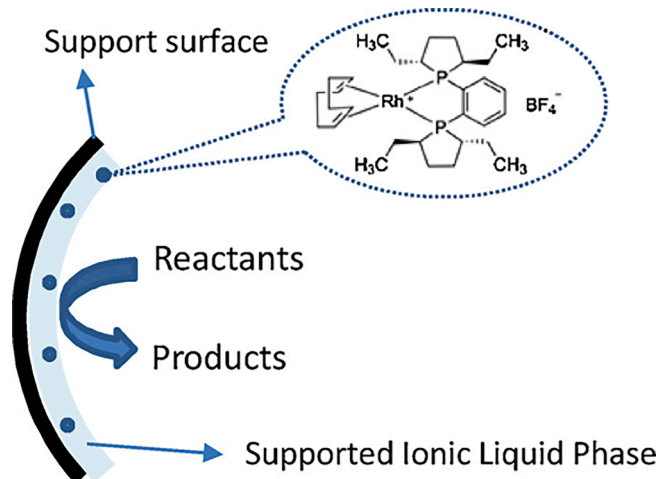


Fig. 6. Scheme of a SILP catalytic system.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ica.2023.121513>.

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