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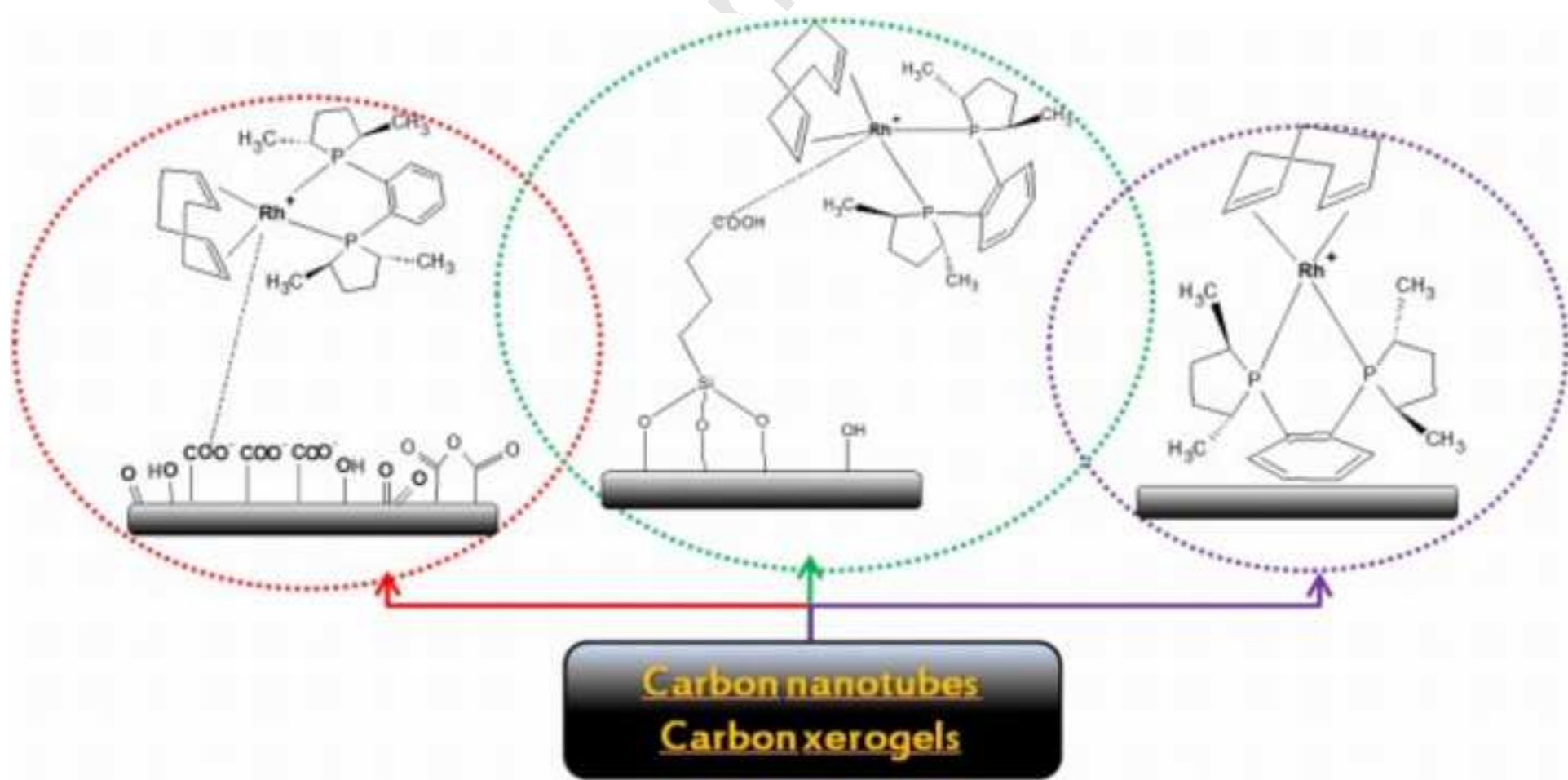
Research highlights

- The chiral catalyst RhDuphos has been anchored on carbon nanotubes and xerogels.
- Non covalent anchoring strategies were used: electrostatic and π-π interactions.
- Supports have been chemically modified to promote desired interactions.
- RhDuphos on an oxidized carbon xerogel is active, enantioselective and reusable.

Non-covalent immobilization of RhDuphos on carbon nanotubes and carbon xerogels.

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Abstract

The immobilization of the chiral complex RhDuphos, by electrostatic or π-π (adsorption) interactions, on carbon nanotubes and carbon xerogels is investigated. To promote such interactions, the supports were either oxidized or heat treated to create carboxylic type surface groups or an apolar surface, respectively. The catalysts were tested in the hydrogenation of methyl 2-acetamidoacrylate.

The prepared hybrid catalysts are less active than the homogeneous RhDuphos, but most of them show a high enantioselectivity and the one prepared with the oxidized carbon xerogel is also reusable, being able to give a high substrate conversion, keeping as well a high enantioselectivity. The anchorage by electrostatic interactions is more interesting than the anchorage by π-π interactions, as the π-π adsorption method produces a modification of the metal complex structure leading to an active hybrid catalyst but without enantioselectivity.

The creation of carboxylic groups on the support surface has led to some hindering of the complex leaching.

Keywords

Hybrid catalysts, rhodium chiral complex, carbon xerogels, carbon nanotubes, hydrogenation.

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1. Introduction

Rh(I) complexes with chiral phospholane ligands, like Duphos (bis-2,5-dialkylphospholano]benzene) or BPE (bis-2,5-dialkylphospholano]ethane), play a pivotal role in catalyzed asymmetric hydrogenations [1]. This kind of ligands can be purchased, but they are rather expensive and consequently their catalytic performance must be optimized. In this and other cases, both, recovery of homogeneous catalysts from the reaction media and reutilization, are highly desirable. Because of that, many approaches to "immobilize" or "anchor" homogeneous catalysts on solid supports are under research. The process, known as heterogenization, leads to hybrid catalysts, so named because they combine the properties of homogeneous and heterogeneous catalysts. In fact, the goal of the heterogenization of homogenous catalysts is to combine the superior activity and selectivity offered by homogeneous catalysts with the ease of separation and recycling of heterogeneous catalysts. This approach is currently an economical, but also a toxicological and environmental challenge. To reach this goal many different strategies have been considered, and they have been the subject of several hundreds of publications, including some reviews and book chapters [2-8]. Usually, heterogenization strategies are classified either as covalent tethering or non-covalent immobilization. In the particular case of the RhDuphos catalyst, the non-covalent immobilization is preferred because the creation of a covalent bond with the support implies a noticeable chemical and structural modification of the complex that strongly influences its chiral induction capacity. For that reason, it is desirable to immobilize the catalyst using electrostatic or Van der Waals forces which do not require a chemical modification of the ligand and impose only slight structural modifications.

A perusal of the literature on this topic shows that the homogeneous catalyst [(R,R)-Me-(Duphos)Rh-(COD)]OTf has been immobilized by the interaction of the triflate counter ion with surface silanols of silica supports (MCM-41) [9], leading to an active and recoverable catalyst. The same complex but with BF_4^- as counterion was immobilized by ion exchange on Al-MCM-41 and Al-SBA-15 [10]. In the first case, the catalyst was very active and enantioselective, with no Rh leaching, while the one prepared with Al-SBA-15 was not stable and significant quantities of Rh were leached during use. However, later Crosman and Hoelderich [11] also reported the heterogenization of [S,S-Me–DuphosRh(COD)]Cl by ionic interactions with the negatively charged Al–M41S or

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Al–SBA-15 frameworks. In both cases, the immobilized catalysts showed high activities and excellent chemo- and enantioselectivities, being as well fully recyclable.

The above commented results show that there are already some positive results in the non-covalent immobilization of the RhDuphos complex in siliceous materials. There is a field open to try to improve the catalysts properties (including economical or technical aspects) by employing other materials as supports.

With the background of literature reviews on the possibilities of carbon materials for the heterogenization of metal complexes [12, 13], and previous own results on the subject [14-16], the present work deals with the non-covalent immobilization of the RhDuphos complex on carbon materials. It must be mentioned that only a few results concerning the immobilization of the RhDuphos complex on carbon materials have been yet reported. They have been obtained by Augustine et al [17], using a heteropolyacid (particularly phosphotungstic acid) to promote the anchoring of the RhDuphos complex. The authors proposed that the hydroxyl groups of the heteropolyacid interact with the support and that the RhDuphos catalyst coordinates to the heteropolyacid through the oxygen atoms on its surface. The obtained catalyst was less active than the homogeneous complex in the hydrogenation of dimethyl itaconate but with comparable enantioselectivity values, and it was reusable.

The present work is focused on the immobilization of the RhDuphos catalyst on two different carbon materials by direct interaction with the support surface, either with support surface oxygen groups or with the carbon basal planes. The selected carbon materials are carbon nanotubes and carbon xerogels, because they are supports which surface can be chemically modified with relative facility and with a suitable porosity to accommodate large molecules and to provide space for large substrates in liquid phase processes. The catalytic properties of the hybrid catalysts have been tested in the asymmetric hydrogenation of methyl 2-acetamidoacrylate (MAA). Enamide hydrogenation is considered a standard test reaction for chiral phosphine ligands. Additionally, it is a very important reaction providing one of the most efficient, cost effective methods for the production of valuable enantiomerically pure-amino acid derivatives. The objective of the work is to prepare an active, selective and stable heterogenized RhDuphos catalyst based on carbon materials by a relatively simple procedure.

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2. Materials and Methods

2.1 Supports

The carbon materials used are:

- Commercial carbon nanotubes (Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences (Timesnano)). Two different samples were used: sample C and sample C_{OH}, which contains a larger amount of surface oxygen complexes, in particular -OH type. Both samples were submitted to a demineralization treatment with HCl solution (HCl 37 wt%, 100 mL/g, stirring, room temperature, 48 h, filtering, washing with distilled water up to pH=7, drying at 373 K). The mineral matter content (remains of the catalyst used in the carbon nanotubes synthesis) was determined by thermogravimetry (10 K/min, up to 1273 K in synthetic air flow (100 cm^3/min)) and expressed as ash wt%. The as-received samples C and C_{OH} contained 1.83 wt% and 4.40 wt% ash, respectively, and this amount was reduced to 0.28 wt% and 1.58 wt%, respectively, after the mentioned treatment. The purified samples were named CD and $C_{OH}D$.

- Two carbon xerogels (CX1 and CX2) of different porous texture, prepared at the Department of Chemical Engineering of the Liège University (Belgium) following the method described in the literature [18, 19]. The samples were grinded and sieved in order to have a particle size between 1.0 and 1.4 mm.

The non-covalent immobilization of the RhDuphos complex on the carbon supports was intended to take place either by electrostatic interactions or by π-π interaction between the aromatic ring of the complex and the support surface. In order to promote the mentioned anchorage, the supports were submitted to several treatments to modify the surface chemistry.

Sample CD was treated in two different ways: A) Oxidation treatment in order to develop oxygen complexes, mainly carboxylic type groups. The treatment was carried out with a saturated solution of $(NH_4)_2S_2O_8$ in H_2SO_4 1M (10 mL solution per gram of solid) at room temperature for 24 hours; afterwards, the sample was washed with distilled water until complete removal of sulfates (test with $BaCl_2$) and dried at 373 K. The sample was named CDS. B) Heat treatment to remove as much as possible surface oxygen groups in order to leave an apolar surface (He flow, 10 K/min up to 1173 K); sample named CDtt.

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Besides, it was considered the possibility of having the surface carboxylic groups away from the support surface in order to avoid any "interference" of the surface. With this purpose carboxylic groups with a hydrocarbon chain were grafted on the support surface. Such a functionalization was done using sample $C_{OH}D$ as shown in Scheme 1 and explained next (step by step).

Step 1. Hydrolysis of the molecule *(3-cianopropyl)triethoxisilane* (named **N**) to transform the nitrile groups into carboxylic groups [20], proceeding as follows: 3 mL of **N** together with 0.78 mL distilled water were stirred at room temperature; then 0.96 mL H_2SO_4 (95-98%) were added slowly (drop by drop, to keep temperature between 333 and 343 K); afterwards, the solution is refluxed (363 K, 24 h) under stirring. After cooling, the organic phase containing the product (named **L**) is collected.

Step 2. Anchorage of species **L** on the $C_{OH}D$ support through the creation of a siloxane type covalent bond by reaction between the triethoxsilane groups of **L** and –OH phenol type groups on the support surface. Procedure: 200 mg of support were added to a mixture of 1 mL (6 mmol/g) of **L** and 5 mL anhydrous methanol and the suspension was left under stirring at 328 K for 20 h. After filtration, the sample, named $C_{OH}DL$, was vacuum dried.
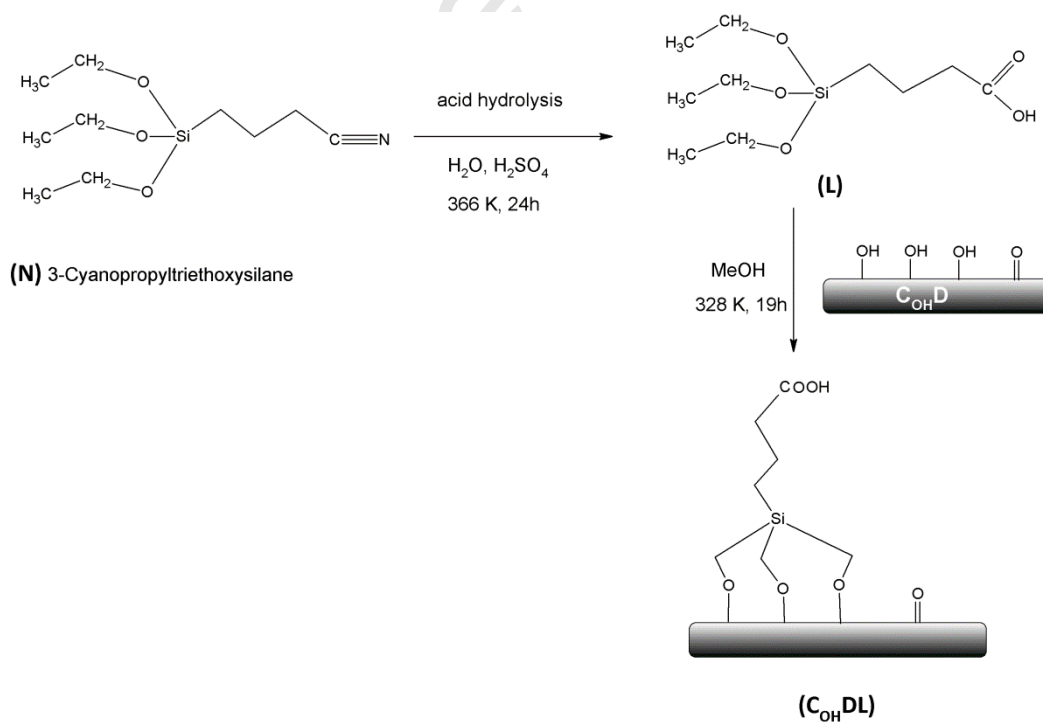
Scheme 1. Preparation and anchorage of the propylcarboxylic acid, for the functionalization of the $C_{OH}D$ nanotubes.

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The carbon xerogel CX2 was also oxidized with the $(NH_4)_2S_2O_8$ solution in the conditions indicated above for the oxidation of sample CD. The oxidized sample is named CX2S.

In summary, the following samples have been used as support: CDS, CDtt, $C_{OH}DL$, CX1, CX2 and CX2S.

2.2. Preparation of catalysts

In a Schlenk system: 200 mg of the support (after outgassing under vacuum at 373 K, 3 h) were put in contact with a solution of the complex ([(Rh((R,R)-Me-Duphos)(COD)]BF$_4$) (20 mg, 0.033 mmol) in anhydrous methanol (5 mL). The suspension was kept in inert atmosphere under stirring at 328 K for 32 h. Then, the catalyst was filtered, washed with methanol (10 x 5 mL) and dried under vacuum at room temperature. The used amounts would give a maximum Rh loading of 1.7 wt%. The catalysts are identified by the support name followed by –RhDuphos.

Scheme 2 shows an overall view of supports and catalyst and the three different proposed interactions between the RhDuphos complex and the supports.
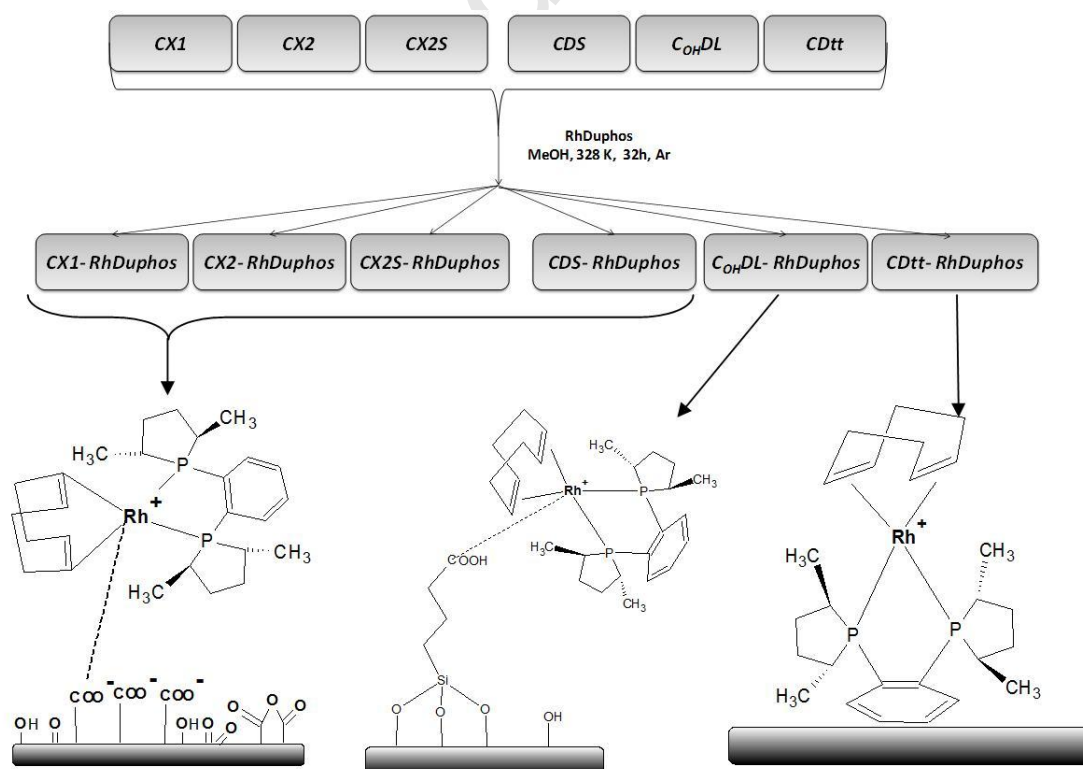
Scheme 2. Nomenclature and anchoring scheme of the hybrid catalysts prepared with the RhDuphos complex.

2.3. Characterization

The textural properties of the supports were analyzed by gas adsorption (N_2 at 77 K and CO_2 at 273 K), using the automatic volumetric apparatus Autosorb-6B (Quantachrome). The samples were previously outgassed at 523 K for 4 h. BET surface area, pore volumes of different size range and pore size distributions have been determined as described in the literature [21].

The study of the surface chemistry was carried out by Temperature Programmed Desorption (TPD), using a thermobalance SDT TA Instruments 2960 coupled to a mass spectrometer Balzers MSC 200 Thermostar. Approximately, 10 mg of sample were heated at 20 K/min up to 1300 K in a 20 cm^3/min He flow. TPD profiles were quantified and also analyzed by deconvolution in order to determine the amount of carboxylic type groups and, in some cases, of phenol type groups. Deconvolution has been carried out using the software Origin 7.0, Gaussian multiple fitting, and considering the decomposition temperatures of the mentioned groups reported in the literature [22, 23].

The rhodium content in the catalysts was determined after metal extraction and analysis of the solution by ICP-OES, using the methodology described in the literature [24]. The catalysts were also characterized by XPS employing a VG-Microtech Multilab 3000 spectrometer.

The samples (supports and catalysts) were also characterized by transmission and scanning electron microscopy, with the equipments JEOL JEM-2010 and HITACHI S-3000N, respectively.

2.4. Catalytic activity and recycling

Reactions were carried out in a stainless steel Parr reactor (40 mL) magnetically stirred (1100 rpm). The reaction vessel is equipped with a gas inlet valve for charging and purging the gas into the reactor and a pressure gauge for the pressure control. The reactor is placed inside a bath with a recirculation water pump and a thermocouple, in order to maintain rigorously the reaction temperature.

In a typical experiment, 30 mg of the hybrid catalyst were introduced in the reactor, along with 7 mL of a MAA solution in anhydrous methanol, of the appropriated

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concentration to obtain a substrate/catalyst ratio close to 350. The reactor was purged first with He and then with H_2 several times and finally the H_2 pressure was set at 5.5 bar. Then, the reactor was placed in the thermostatic bath at the selected temperature of 296 K.

The homogeneous process was carried out using 3 mg (5 μmol) of the RhDuphos complex and keeping all the conditions as indicated above.

A blank test (without catalyst) was also carried out. In this case, no conversion was observed in 10 h.

Reactants and products were analyzed by gas chromatography using the HP 6890 equipment with a FID detector and a CP-1Chirasil-L-Val column (25 m x 250 μm x 0.12 μm).

Recycling tests were carried out as follows: after a catalytic run, the catalyst was separated from the reaction media by decantation and solvent removal with a syringe; taking care to keep the catalyst in an inert atmosphere all the time. Afterwards, a new substrate solution in 7 mL of anhydrous methanol was added quickly, and the catalytic run was started under the same conditions.

3. Results and discussion

3.1. Supports characterization

Porous texture

The N_2 adsorption isotherms (77 K) are provided in the supplementary information (Fig. SI1).

Table 1 includes the calculated surface area and porosity parameters. These data show that the supports used have different textural properties.

Table 1. Textural properties of the carbon supports.

Sample	S_{BET} [a] $[m^2/g]$	S_{ext} [b] $[m^2/g]$	$V_{\mu t}$ [c] $[cm^3/g]$	$V_{u\mu}$ [d] $[cm^3/g]$	$V_{s\mu}$ [e] $[cm^3/g]$	V_{meso} [f] $[cm^3/g]$
CD	173	160	0.07	0.04	0.03	0.54
CDS	165	158	0.07	0.04	0.02	0.52
CDtt	174	159	0.07	0.04	0.03	0.54
CX1	624	275	0.29	0.24	0.06	0.66
CX2	593	255	0.28	0.23	0.05	0.24

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| | CX2S | 526 | 198 | 0.25 | 0.20 | 0.05 | 0.18 |

[a] S_{BET} - BET surface area, [b] S_{ext} - external surface, [c] $V_{\mu t}$ - total micropore volume, [d] $V_{u\mu}$ – narrow micropore volume, [e] $V_{s\mu}$ - supermicropore volume, [f] V_{meso} - mesopore volume (calculated between 0.2-0.97 P/P^0).

Carbon nanotubes are mainly mesoporous materials, as their porosity consists in the inner cavity of the nanotube and pores formed by the interaction of isolated nanotubes, with a low BET surface area. On the other hand, carbon xerogels contain a significant contribution of both micro- and mesopores and a higher BET surface area. There are, however, some differences between the isotherms of the two carbon xerogels (in particular, regarding the slope and the hysteresis loop), what reveals differences in the porous structure of these two samples (see Figure SI1).

It can be observed (Table 1) that the textural properties of sample CD are not modified upon the oxidation and heat treatments (samples CDS and CDtt, respectively). Carbon xerogels CX1 and CX2 mainly differ in the mesopore volume and the oxidation treatment of sample CX2 produces a small reduction of the pore volumes.

It should be taken into account that the degassing treatment carried out prior to the N_2 adsorption measurements removes some carboxylic type surface oxygen groups and this could have modified slightly the textural properties of the oxidized supports.

Surface chemistry

The TPD profiles obtained for all the supports are provided as supplementary information (Fig. SI2). Table 2 shows the TPD data including amount of CO and CO_2 evolved (in μmol/g), total oxygen (in wt%) and phenol and carboxylic type groups determined by deconvolution of the CO and CO_2 desorption profiles, respectively. Data of samples CD and $C_{OH}D$, have been included as a reference to analyze the effect of the functionalization treatments.

Table 2. Surface chemistry of the carbon supports determined by TPD.

Sample	CO [a] [μmol/g]	CO_2 [a] [μmol/g]	O [b] [wt%]	Phenol [c] [μmol/g]	Carboxylic [d] [μmol/g]
CD	575	218	1.6	18	21
CDS	835	605	3.3	118	279
CDtt	67	44	0.2	21	0
$C_{OH}D$	1359	306	3.2	989	47
$C_{OH}DL$	911	271	2.3	615	73

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CX1	860	505	3.0	38	180
CX2	1067	474	3.2	210	185
CX2S	2514	1777	9.7	1446	779

[a] CO and CO_2 evolved (µmol/g), [b] oxygen weight percentage (%), [c] amount of phenol type groups (µmol/g) calculated by deconvolution of the CO desorption profile, [d] amount of carboxylic acid type groups (µmol/g) calculated by deconvolution of the CO_2 desorption profile.

Oxidation of sample CD with the $(NH_4)_2S_2O_8$ solution produces a noticeable development of surface oxygen groups (O wt% from 1.6 to 3.3%), that supposes an increase in the amount of carboxylic type groups of one order of magnitude from 21 to 279 µmol/g.

As expected, sample CDtt has a very low amount of surface oxygen groups.

Because tethering of molecule L takes place by reaction with –OH phenol surface groups, this reaction should lead to a reduction of the amount of phenol type groups after tethering of L (Scheme 1) and this is confirmed by the TPD data. Besides, the increase of the carboxylic type groups is, as well, observed.

Regarding the carbon xerogels, samples CX1 and CX2 show a similar surface chemistry while sample CX2S contains a noticeably larger amount of oxygen; in particular and in relation with the purpose of the treatment, a large amount of carboxylic type groups have been created.

It can be mentioned that under the same oxidation conditions, the carbon xerogel shows a much more important development of surface groups than the carbon nanotubes. This confirms the lower reactivity of the carbon nanotubes, previously reported by Gomes et al. [25].

3.2. Catalysts characterization

The amount of Rh loaded in the catalysts is shown in Table 3. It is lower than the possible maximum amount according to the quantities used in the catalysts preparation (1.7 wt%, 165 µmol/g). Supports CDS, CX1, CX2 and CX2S, in which the anchorage of the complex is assumed to occur by electrostatic interactions, contain enough carboxylic type surface groups to anchor the 165 µmol/g of Rh complex used in the preparation (see Scheme 2 and Table 2). Thus, the lower metal loading means that some surface groups are not accessible or not able to interact with the cationic Rh complex. In the case of support $C_{OH}DL$, however, there is a good agreement between the amount of surface carboxylic groups and the amount of loaded Rh. It should be also pointed out

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that the support with the "clean" surface (CDtt) leads to the highest Rh loading indicating that π-π interactions are favored.

Table 3. Rh amount and XPS analysis data of the fresh hybrid catalysts.

Sample	Rh [wt%]	Rh [μmol/g]	XPS data				
			Rh 3d$_{5/2}$	P 2p	P/Rh	Rh/C	F [a]
RhDuphos			308.81	131.6	2		
CDS-RhDuphos	0.60	58	-	-	-	-	-
C$_{OH}$DL-RhDuphos	0.74	72	309.20	131.9	0.7	0.002	3
CDtt-RhDuphos	1.01	98	309.70 (80%) 307.90 (20%)	131.9	1.5	0.001	2
CX1-RhDuphos	0.61	59	308.47	132.0	0.4	0.010	10
CX2-RhDuphos	0.41	40	308.81	131.8	0.2	0.016	25
CX2S-RhDuphos	0.33	32	308.47	131.5	0.3	0.010	20

[a] F: quotient between the Rh/C ratio determined by XPS (surface ratio) and the Rh/C ratio determined by ICP (total ratio)

The obtained XPS spectra of the supported RhDuphos complex can be found as supplementary information (Figure SI3). The corresponding XPS data are shown in Table 3, where data obtained for the unsupported complex are also included.

Binding energy of Rh3d$_{5/2}$ corresponds to Rh (I), while P2p B.E. corresponds to P in phosphine [26, 27], indicating that the heterogenized complex keeps the electronic state of the original molecule. In the case of sample CDtt-RhDuphos the binding energy corresponding to Rh(0) is also observed (307.9 eV), and the proportion of this species is about 20%. In this case, reduction of Rh occurs by the extensive interaction of the complex with the carbon basal planes of the "clean" nanotubes surface. The atomic P/Rh ratio is, in all cases, noticeably lower than that corresponding to the RhDuphos molecule; this indicates that a modification of the Rh coordination sphere has occurred upon anchoring and some ligand molecules are lost. With basis on the P/Rh ratio and assuming that the amount of P determines the amount of RhDuphos complex, it can be inferred that the active Rh species are much less than those indicated by the Rh loading.

Parameter F (Table 3) is the quotient between the Rh/C ratio determined by XPS (surface ratio) and the Rh/C ratio determined by ICP (total ratio). The calculated F values give an indication of the location of the Rh species [24]. As a larger value of F corresponds to a more external location, the data indicate that the support properties

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largely affect this aspect; the distribution of the Rh species is more homogeneous in carbon nanotubes than in carbon xerogels.

TEM analysis

With the exception of sample CDtt-RhDuphos, the TEM images of the hybrid catalysts are similar to those of the supports, meaning that the supported active phase is a set of well distributed complex molecules. As an example, Figure 1 shows micrographs of catalyst CDS-RhDuphos.
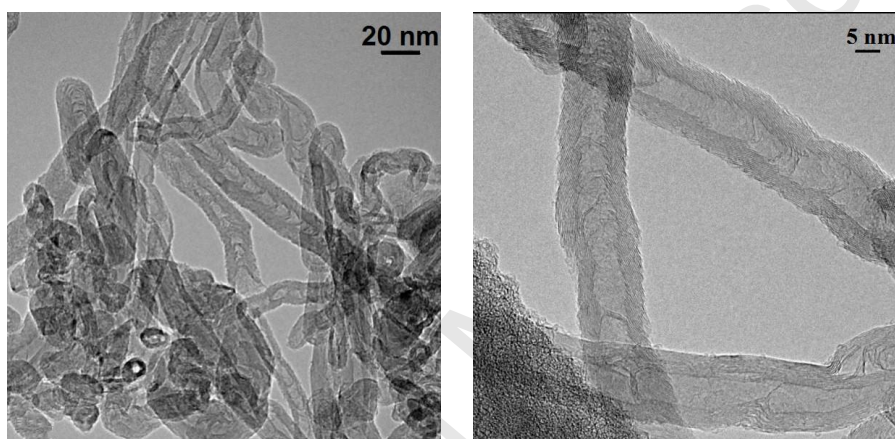

Figure 1. TEM images of the CDS-RhDuphos fresh catalyst.

In contrast, the TEM analysis of catalyst CDtt-RhDuphos (Figure 2) reveals the presence of some small particles (average size is 2 nm). This result is in agreement with the presence of Rh(0) determined by XPS and indicates that this support aids the reduction of the Rh complex.
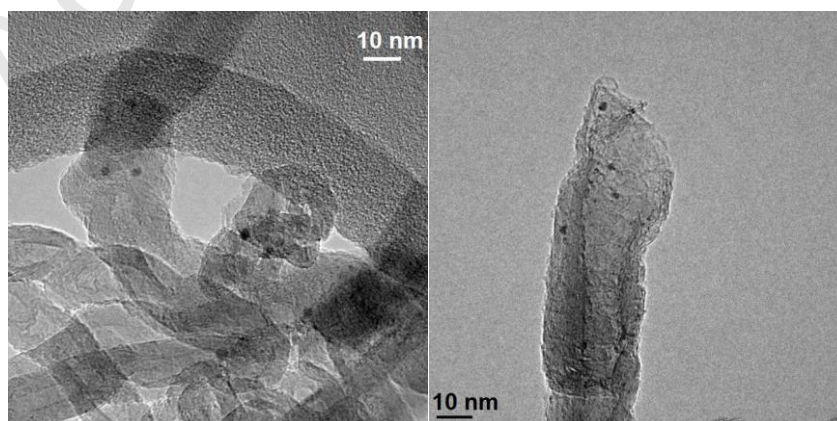

Figure 2. TEM images of the CDtt-RhDuphos fresh catalyst.

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3.3. Catalytic activity and enantioselectivity

Table 4 shows the catalytic activity and selectivity data obtained with the homogeneous and the hybrid catalysts in the MAA hydrogenation. Conversion, TOF and enantiomeric excess correspond to the time indicated in each case. The amount of Rh used in each test (as supported species) is also included.

Table 4. Catalytic activity and selectivity data in the first reaction run of MAA hydrogenation.

Sample	μmol Rh [a]	t [b] [h]	Conversion [c] [%]	TOF [c] [h⁻¹]	e.e.(R) [d] [%]
RhDuphos	5	2.2	100	111.6	100
CDS-RhDuphos	1.7	10	45	21.6	100
C$_{OH}$DL-RhDuphos	2.2	22	50	7.2	100
CDtt-RhDuphos	2.9	3	100	72.0	4.5
CX1-RhDuphos	1.8	22	64	7.9	100
CX2-RhDuphos	1.2	22	50	9.4	100
CX2S-RhDuphos	1.0	22	27	5.4	100

[a] μmoles of Rh in each test, [b] reaction time (hours), [c] conversion (%) and turn-over frequency (TOF) (h⁻¹) values, [d] enantiomeric excess for the R-isomer (%).

With the exception of sample CDtt-RhDuphos, the hybrid catalysts show a 100% enantioselectivity, but they are noticeably less active than the homogeneous catalyst.

The lower catalytic activity suggests that not all the Rh complex molecules loaded constitute active species or are not accessible. Moreover, diffusion limitations inherent to the anchorage of the complex in a porous solid are another potential factor to explain the lower activity, but this approach has yet to be confirmed by the corresponding kinetic studies.

The lower catalytic activity can, in a first approach, be explained by diffusion limitations inherent to the anchorage of the complex in a porous solid, but it has to be considered also that, as indicate before, probably not all the Rh atoms loaded constitute active species.

Although very active, catalyst CDtt-RhDuphos shows a very poor enantioselectivity. This behavior could be due to the presence of metallic particles and also to the fact that the π-π interaction between the aromatic ring of the complex and the support surface

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leads, likely, to an important modification of the complex structure that decreases its enantioselective capacity.

Comparing the behavior of samples CDS-RhDuphos and $C_{OH}DL$-RhDuphos it can be concluded that having the carboxylic type groups apart of the surface does not improve the catalyst properties.

A comparison of TOF values shows that catalyst CX2-RhDuphos is more efficient than CX1-RhDuphos. A similar support effect was observed previously in the hydrogenation of carvone using a Rh diamine complex supported in the same carbon xerogels [15]. Such an effect was explained by the different location of the Rh complex in both supports, being more externally located in CX2Ox-Rh (F=35) than in CX1Ox-Rh (F=16) and because of that diffusion limitations are lower. The F values obtained for CX1-RhDuphos (10) and CX2-RhDuphos (25) are consistent with that hypothesis to explain the differences in activity between these two catalysts.

Catalyst CX2S-RhDuphos is however less active, but in this case the surface chemistry may also play a role. In previous works [28], a significant effect of the support surface chemistry on the activity of the hybrid catalysts was found, as a large amount of oxygen groups, particularly carboxylic acid type, led to a lower catalytic activity. To interpret this effect it can be considered that a rich surface chemistry hinders the access of the reagents to the active centre.

In any case, the interpretation of these results must be linked to the analysis of Rh leaching from the catalysts. The Rh content and the Rh leaching (in %) have been determined after the first catalytic run, and the obtained data are compiled in Table 5. These data indicate that leaching is an important problem and the support properties affect the stability of the anchored complex. Catalysts prepared with the oxidized supports (CX2S-RhDuphos and CDS-RhDuphos) are more stable against leaching. On the other hand, catalyst CDtt-RhDuphos suffers a very important leaching after the first run.

The solution removed from the reaction vessel (separated from the solid catalyst) was used in a new catalytic run by adding fresh substrate. In all cases conversion was negligible (less than 3% in 22 h). This indicates that the leached species are not active and thus, the catalytic activity of the hybrid catalysts is due to the supported complex.

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3.4. Recycling

Figure 3 shows conversion and e.e. data obtained in several consecutive catalytic runs carried out with the carbon nanotubes based catalysts.
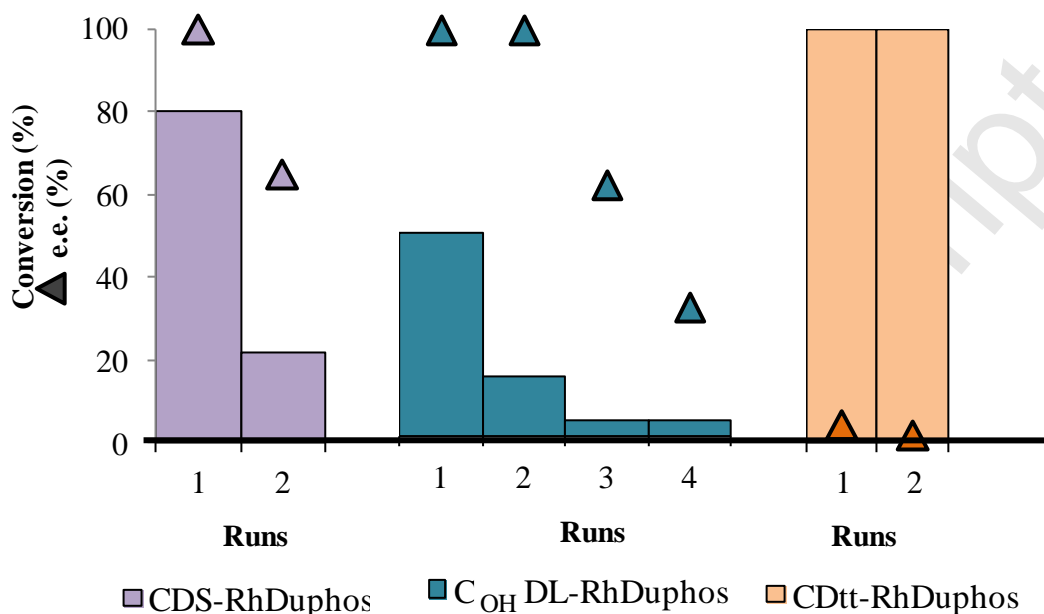

Figure 3. Conversion (%) and e.e. (%) in consecutive catalytic runs for catalysts based on carbon nanotubes (CDS-RhDuphos (t=22 h), C_{OH}DL-RhDuphos (t=22 h) and CDtt-RhDuphos (4h)). (30 mg catalyst, 7 mL MAA anhydrous methanol solution, S/C ≈ 350, P(H_2)= 5.5 bar, T= 296 K).

Data of Figure 3 show that catalysts CDS-RhDuphos and C_{OH}DL-RhDuphos suffer an important loss of activity and enantioselectivity in consecutive runs. The important conversion decrease is not explained by the Rh leaching after the first run (see Table 5) and thus it can be concluded that these catalysts are strongly deactivated. In the case of sample CDtt-RhDuphos, in spite of the 52% Rh leaching, conversion is very high (100% in only 4h) but the catalyst is not enantioselective at all. This result indicates that the state of the Rh species is very different in support CDtt compared to CDS and C_{OH}DL. Due to the low selectivity of these catalysts, they were not tested in further catalytic runs.

Figure 4 shows analogous recycling data corresponding to catalysts prepared with carbon xerogels.

In this case, there is also some decrease in conversion with consecutive runs but the enantioselectivity is highly preserved.

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Catalyst CX1-RhDuphos loses about 80% of its activity from run 1 to run 5, while activity loss is much lower in the case of samples prepared with supports CX2 and CX2S.
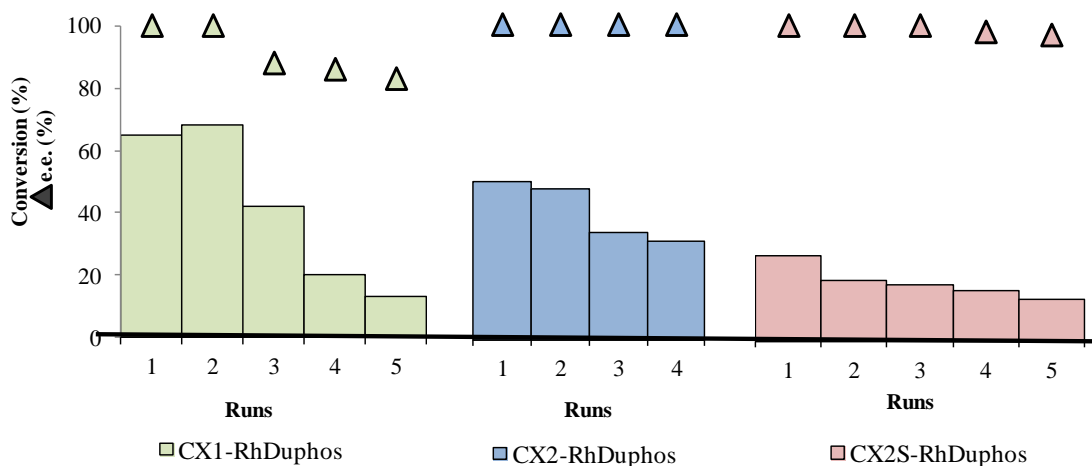

Figure 4. Conversion (%) and e.e. (%) in consecutive catalytic runs for catalysts based on carbon xerogels (each run t=22 h). (30 mg catalyst, 7 mL MAA anhydrous methanol solution, S/C ≈ 350, P(H_2)= 5.5 bar, T= 296 K).

Rh content and Rh leaching, after each catalytic run, are included in Table 5.

Table 5. Rh amount of the fresh and used hybrid catalysts.

Sample	Use	Rh wt [%]	Leaching [%]
CDS-RhDuphos	Fresh	0.60	-
	After run 1	0.46	23
	After run 2	0.44	3
C_{OH}DL-RhDuphos	Fresh	0.74	-
	After run 1	0.50	32
	After run 2	0.42	11
CDtt-RhDuphos	Fresh	1.01	-
	After run 1	0.48	52
	After run 2	0.30	18
CX1-RhDuphos	Fresh	0.61	-
	After run 1	0.41	33
	After run 2	0.29	19
	After run 3	0.27	3
	After run 4	0.26	1
CX2-RhDuphos	Fresh	0.41	-
	After run 1	0.27	34
	After run 2	0.14	32

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	After run 3	0.14	0
	After run 4	0.14	0
CX2S-RhDuphos	Fresh	0.33	-
	After run 1	0.26	21
	After run 2	0.22	12
	After run 3	0.22	0
	After run 4	0.22	0

Data corresponding to catalysts prepared with the carbon xerogels show that after use in a second run the leaching process seems to stop. That is, the catalysts reach a stable Rh loading.

In the case of the catalysts prepared with supports CX2 and CX2S, conversion is kept in spite of the Rh loss (meaning a TOF increase). This could mean that part of the anchored (and leached) Rh species were not active, supporting the previous suggestion.

Because of its higher stability against leaching and also in conversion and enantioselectivity, catalyst CX2S was selected to do a longer term test and to state if a higher conversion with a high enantioselectivity could be attained. This study is presented in the next section.

3.5. Longer term study with catalyst CX2S-RhDuphos

Figure 5 shows the variation of conversion and enantioselectivity versus time, determined for catalyst CX2S-RhDuphos in two long term consecutive catalytic runs (Figure 5a corresponds to run 1 and Figure 5b to run 2).
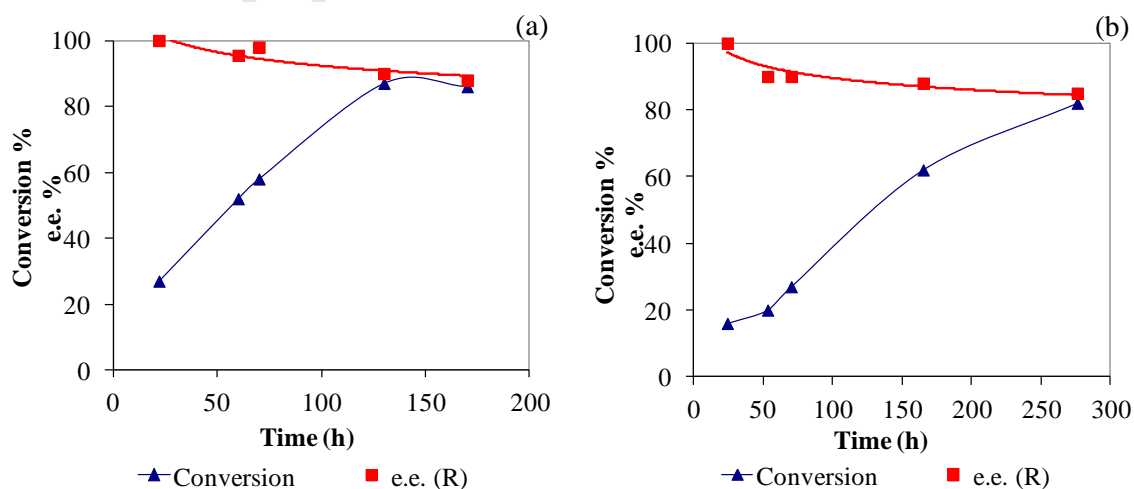

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Figure 5. Conversion (%) and e.e. (%) versus time for catalyst CX2S-RhDuphos: a) run 1, b) run 2. (30 mg catalyst, 7 mL MAA anhydrous methanol solution, S/C ≈ 350, P(H$_2$)= 5.5 bar, T= 296 K).
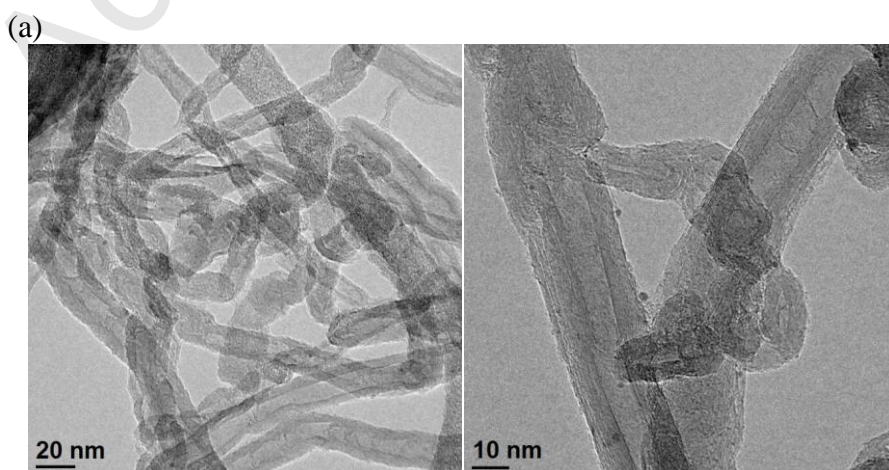
It can be observed that catalyst CX2S-RhDuphos is able to give a high substrate conversion keeping as well a high selectivity. Upon recycling (Fig 5b), the catalyst becomes less active, but it is also possible to achieve a high conversion with a high enantioselectivity. After the first run (175 h) leaching was 13% and after the second one (276 h) it was only an extra 2%, meaning that this catalyst can be considered stable.

3.6. Characterization of used catalysts

The hybrid catalysts have been analyzed by XPS after the first catalytic run and by TEM after several runs. The Rh3d$_{5/2}$ XPS spectra obtained are provided as supplementary information (Fig. SI4). For the sake of comparison, figures include also the XPS profiles of the corresponding fresh catalyst.

No XPS signals are observed for catalyst CDtt-RhDuphos, meaning that the Rh species are not accessible to the X-ray radiation, while no variation of the Rh 3d$_{5/2}$ and P2p binding energies has been observed in the other catalysts. There is, however, some reduction of the surface atomic P/Rh ratio, together with some increase of the F value ((Rh/C)$_{XPS}$/(Rh/C)$_{ICP}$). These observations indicate that the anchored complex suffers some modifications upon use, but the available data do not allow a precise definition of them.

Figures 6a, 6b and 6c show, as an example, TEM images obtained for used catalysts C$_{OH}$DL-RhDuphos, CX1-RhDuphos and CX2S-RhDuphos, respectively.
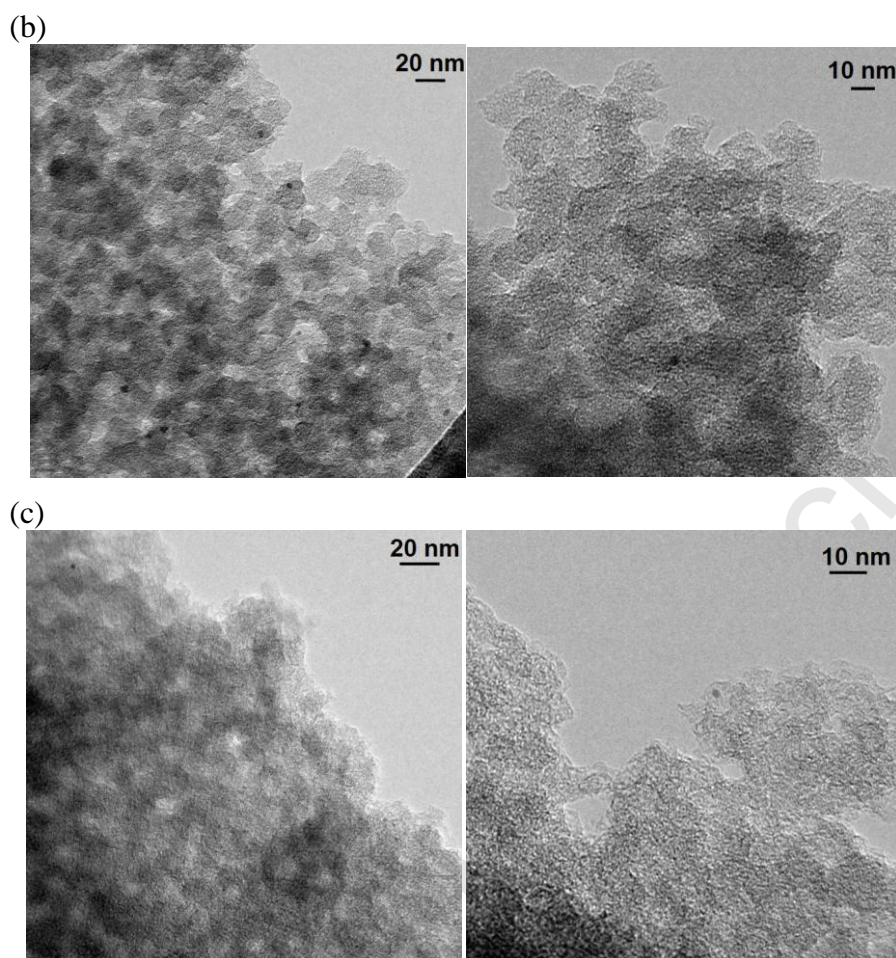

(a)

20 nm   10 nm

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Figure 6. TEM images of used catalysts: a) C$_{OH}$DL-RhDuphos, b) CX1-RhDuphos and c) CX2S-RhDuphos.

It can be observed that after use in several runs a few small metallic particles are formed. Taking into account that after the first catalytic run the catalysts do not contain Rh(0), as indicated by the XPS analysis, it can be concluded that the complex reduction occurs very slowly. The results also show that the development of metallic particles depends on the support used. It must be pointed out that catalyst CX2S-RhDuphos after the two consecutive long term runs (about 450 h) shows a very low amount of metallic particles and this can be behind the high selectivity kept by this catalyst.

The formation of a larger amount of metallic particles was observed in a previous work [15] in which hybrid catalysts were prepared with the same carbon xerogels and a Rh diamine complex, and they were used for the hydrogenation of cyclohexene and carvone at 333K and P=10-20 bar. The data obtained now indicate thus, that the reduction of the hybrid catalysts is highly dependent on the Rh complex, but also on the reaction conditions and that mild reaction condition are necessary to preserve the complex.

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4. Conclusions

The following main conclusions have been derived from the results presented and discussed above.

The homogeneous chiral catalyst RhDuphos has been immobilized on carbon nanotubes and carbon xerogels by non covalent anchoring strategies: electrostatic and π-π interactions.

Most of the obtained hybrid catalysts are active and enantioselective. Activity is, however, lower than that of the very effective RhDuphos complex in homogeneous phase. This can be explained by modifications of the coordination sphere upon anchoring and likely to diffusion limitations.

The anchorage of the commercial RhDuphos complex on carbon materials by electrostatic interactions is more interesting than the anchorage by π-π interactions.

Leaching is an important drawback of the prepared catalysts, but the creation of carboxylic groups on the support surface hinders leaching to some extent.

The hybrid catalyst prepared with the oxidized carbon xerogel CX2S has shown to give a high conversion and enantioselectivity in long term experiments, being as well recyclable.

Acknowledgements

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