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Heterogenization of a chiral molecular catalyst on a carbon support using tryptophan as anchor molecule

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Abstract: The (R,R)-RhDuphos chiral catalyst has been heterogenized on the surface of a carbon material with the aid of L-tryptophan (Trp) as anchor molecule. Trp is effectively adsorbed on the carbon surface through its arene unit and is able to coordinate Rh by means of the carbonyl and amine functional groups. The chiral hybrid catalysts prepared are very active for the asymmetric hydrogenation of 2-methyl-acetamidoacrylate with an acceptable enantioselectivity. Besides, when prepared with a high Trp/Rh ratio they have shown to be stable and reusable.

Immobilization of homogeneous molecular catalysts on solid supports allows to combine the main advantages of homogeneous and heterogeneous catalysis (high activity and selectivity, and easiness to recover and reuse the catalyst, respectively) and renders what is known as heterogenized or, also hybrid, catalysts [1–5]. Among the several immobilization methods reported [2], those based on a non-covalent interaction of the molecular catalyst with the support would hinder chemical and structural modifications of the active species. Because of that they are preferred, in particular if the purpose is the heterogenization of a molecular chiral catalysts [6,7]. However, a strong and direct adsorption on the support surface can have, as well, detrimental consequences for the immobilized molecular catalyst, and thus intermediate linkers with specific functionalities affine to the support surface and able to act as a ligand of the metal complex are sometimes used. Such species are known as “anchor” molecules.

The present work focuses on the immobilization of the well-known chiral catalyst complex 1,2-bis[(2*R*,5*R*)-2,5-dimethylphospholano] benzene(1,5-cyclooctadiene)rhodium(I) tetrafluoroborate (abbreviated here as (R,R)-RhDuphos)^[8] on a carbon material (carbon black), using L-tryptophan as anchor molecule. Carbon materials have a high potential for this application as they can be prepared with a large variety of textural properties, surface chemistry and morphology [4,5,9,10]. This proposal is inspired by the AC/Ar-S-F systems developed by Godino-Salido et al. [11] and López-Garzón et al. [12] in which Ar is a planar heteroaromatic residue, modified with designed pendant functions (F) through a polymethylene chain (S), and adsorbed on the surface of an activated carbon (AC) by π - π interactions. It has been reported that these interactions imply irreversible electron donation from the carbon surface to a vacant π orbital of the molecule [13]. Fundamentals of this kind of interaction have been reported recently [14]. Systems similar to those described above have been used to adsorb metal ions from aqueous solutions [15,16]. Catalyst immobilization by π - π stacking on carbon nanotubes, graphene oxide and carbon beads has been recently

reported by Cunillera et al. [17] but developing modified ligands bearing a pyrene moiety.

Tryptophan (Fig. 1) contains an arene unit connected, through a short aliphatic fragment, to carbonyl and amine functional groups that can act as ligands to coordinate Rh and bind the phospholane complex.

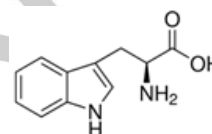


Figure 1. Molecular structure of L-tryptophan

Experimental

The carbon material used as support to prepare the hybrid chiral catalysts is the commercial high-surface area carbon black T-1015 (Columbian Chemical Company, USA), that has been treated at 2000 °C in Ar atmosphere and named T2 in this work. The aim of the high temperature heat treatment is to reduce the surface polarity to favor the adsorption of the tryptophan arene unit. As expected, carbon T2 contains almost no surface oxygen groups and its main textural properties are: 369 m²/g specific surface area, 1.74 cm³/g total pore volume and 1.50 cm³/g mesopore volume [18].

The first step of this study is to determine if carbon T2 is able to adsorb enough tryptophan (Trp) to anchor the amount of Rh complex corresponding to 1 wt% (97 μ mol/g) loading. For this purpose an aqueous solution of Trp is put in contact with a degasified sample of T2 (1 mL/mg) in a continuously shaken water bath at 25 °C during 4 days and afterwards the suspension is left to rest for 7 days more. This method has been adapted from the literature [15]. Solutions of four different Trp concentrations have been used: 0.1*10⁻⁴ M, 1.9*10⁻⁴ M, 3.9*10⁻⁴ M and 7.8*10⁻⁴ M, which correspond, respectively, to Trp/Rh molar ratios of 1, 2, 4 and 8. After the contact time, the samples are filtered and the solution is analysed by UV-Vis spectrophotometry (absorbance maximum at 288 nm). All samples were prepared by duplicate and they are named T2-Trp-x, where x=1, 2, 4, 8, makes reference to the Trp/Rh ratio.

The stability of the samples against Trp leaching was evaluated by studying the potential Trp desorption. About 30 mg of each T2-Trp-x sample were put in contact with 7 mL distilled water, the mixture was stirred at 25 °C for 1.5 h, then it was filtered and the solution analyzed by UV-Vis spectrophotometry.

The results of the adsorption-desorption behavior of tryptophan on the used carbon black are line with those reported for the adsorption of this molecule on activated carbon [19].

Each T2-Trp-x sample was put in contact with an aqueous solution (290 mL per gram of solid) of (R,R)-RhDuphos of the

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appropriate concentration to obtain a nominal 1 wt% Rh in the catalyst. A glove-box was used to prepare the solution and to carry out the impregnation. The samples remain at room temperature, under agitation, until the original dry aspect of the carbon material is restored. The actual amount of loaded Rh complex was determined by ICP-OES (Inductively Coupled Plasma-Optical Emission Spectroscopy). The catalysts are named T2-Trp-x-Rh.

They were tested in the asymmetric hydrogenation of 2-methyl-acetamidoacrylate (MAA) (Fig. 2). The reactor was loaded inside the glove box with 30 mg hybrid catalyst, 100 mg substrate and 7 mL water (S/C close to 250). Then, the closed reactor was moved to the reaction place, where it was kept at 25 °C, purged, and pressurized with 5.5 bar H₂. The reaction was performed, under stirring, for 3 h. To study the catalyst reutilization, once finished the catalytic run, the mixture was centrifuged and the solution removed, then the fresh substrate was added and a second catalytic run was started with the procedure and conditions indicated above.

After each catalytic run, the solid and liquid phases were separated by filtration. The solution was submitted to an extraction process (5 x 2 mL diethyl ether), and the extracts were analysed by gas chromatography (HP6890 Series II, column CP-1 Chirasil-L-Val 25 m x 250 μm x 0.12 μm). The sample for analysis contained 490 μL of the problem solution and 10 μL of 73000 ppm decane solution (internal standard) in acetone.

A homogeneous phase test was carried out in the same conditions but with 0.0017 g of (R,R)-RhDuphos dissolved in the substrate solution.

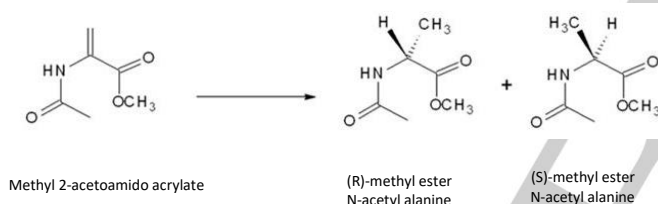


Figure 2. Hydrogenation of 2-methyl-acetamidoacrylate (MAA).

Results

Table 1 shows data of Trp adsorption on carbon T2 as determined from UV-Vis analysis of the solution after impregnation. The value in brackets is the % of Trp removed from the impregnation solution.

Table 1. Tryptophan adsorption on the carbon support in stability tests, and Rh leached in used catalysts.

Sample	Adsorbed Trp (μmol/g) ^[a]	Rh leached ^[b] (%)
T2-Trp-1	95.7 (100%)	
T2-Trp-2	193 (100%)	6.6
T2-Trp-4	365 (94%)	5.3
T2-Trp-8	544 (70%)	0.3

[a] Calculated from UV-Vis measurements, the value in brackets is the percentage of Trp removed from solution by adsorption on carbon T2 (see the text for details).

[b] for T2-Trp-x-Rh catalysts, expressed as % of the original Rh loading lost after the catalytic activity test.

Assuming a 1:1 stoichiometry for the coordination of the Rh complex to the anchored Trp, the results of Table 1 indicate that all samples contain enough Trp to prepare the desired hybrid catalysts with 1 wt% Rh (97 μmol/g).

The desorption study shows that the Trp concentration in the solution is very low, below the detection limit of the technique. This means that the maximum amount of leached Trp could be 0.03% of the Trp adsorbed and indicates that samples T2-Trp-x are very stable against leaching.

The Rh loading in the T2-Trp-x catalysts, determined by ICP-OES, is about 0.98 wt% in all the samples and thus, it can be concluded that the prepared catalysts contain the desired Rh amount.

The binding energy of Rh 3d_{3/2} determined by XPS is about 309.7 eV. This value is higher than the one corresponding to Rh in the (R,R)-RhDuphos complex (308.8 eV)^[20] what is likely a consequence of the coordination of Rh with electronegative atoms like O and N from Trp.

Rh loading in most of the used catalysts has been also determined by ICP-OES. Leaching has been calculated and expressed as % of the initial Rh loading that has been removed from the hybrid catalyst (Table 1). It can be observed that Rh leaching is low and it decreases as the amount of anchored Trp increases. This means that an excess of Trp must be present on the carbon surface to assure the proper interaction of the Rh complex with the anchor molecule.

Table 2 shows results of MAA conversion and enantiomeric excess (ee) to the R isomer.

Table 2. MMA conversion and enantiomeric excess in the catalytic activity tests^[a] carried out.

Sample	MMA conversion (%)	ee (%) ^[b]
T2-Trp-1-Rh	84	49
T2-Trp-2-Rh	94	60
T2-Trp-4-Rh	95	59
T2-Trp-8-Rh	97	43
T2-Trp-8-Rh run 2	100	41
Homogeneous	100	100

[a] 30 mg hybrid catalyst, 100 mg substrate, 7 mL water, 5.5 bar H₂, 25 °C, 3 h

[b] ee to the R isomer

Data of Table 2 show that hybrid catalysts prepared using L-tryptophan as anchor molecule are very active for MAA hydrogenation, being the substrate conversion in most cases close to 100%. These results show that the (R,R)-RhDuphos complex maintains its high catalytic activity when it is anchored on the T2 surface. The e.e. values obtained with the hybrid catalysts range between 40% and 60%, and although they are lower than the high value given by the homogeneous complex, it can be stated that the purpose of keeping the chirality of the Rh complex upon heterogenization has been achieved in a considerable extent. As Rh leaching is very low, almost negligible in the case of sample T2-Trp-8-Rh (Table 1), it can be considered

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that the homogeneous phase catalytic process contribution in the data reported in Table 2 is not significant.

Catalyst T2-Trp-8-Rh has been reused following the procedure explained in the experimental section and it has been found that activity and selectivity are completely preserved in the second run (Table 2). This can be considered as a proof of the reusability of the catalysts prepared using the anchoring method proposed in this work.

Conclusion

Chiral hybrid (heterogenized) catalysts have been prepared using L-tryptophan (Trp) to anchor the (R,R)-RhDuphos complex to the surface of a heat treated carbon black. Trp is effectively adsorbed on the carbon surface and a molar excess of adsorbed tryptophan respect to the desired molar Rh loading (Trp/Rh ratio of 8) leads to very stable catalysts against leaching of the Rh complex. The prepared hybrid catalyst are very active and the supported complex keeps an acceptable enantioselectivity. Besides, this kind of catalysts has shown to be reusable. This simple and cost-effective preparation procedure allows to prepare active and stable catalysts and opens the door for a more exhaustive study including the effect of tryptophan chirality and reaction conditions (temperature, pressure, etc.) in order to improve the catalysts enantioselectivity.

Acknowledgements

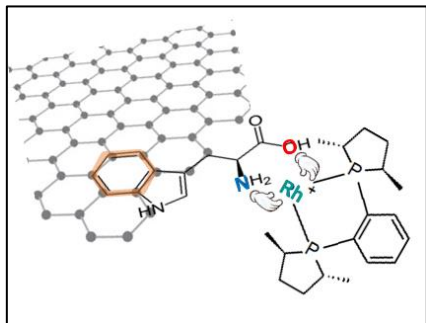
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Keywords: (R,R)-RhDuphos • carbon material • L-tryptophan • heterogenization • asymmetric hydrogenation

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The chiral homogeneous catalyst (R,R)-RhDuphos has been tethered to a carbon black support using L-tryptophan as “anchor” molecule. It bears an aromatic ring with a high affinity to the support surface and N- and O- atoms to coordinate the metal center. This is a non-covalent anchorage aimed to preserve the catalytic properties of the molecular catalyst.

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