Effects of confinement in hybrid diamine-Rh complex-carbon catalysts used for hydrogenation reactions

L. J. Lemus-Yegres, M. C. Román-Martínez^{*}, I. Such-Basáñez,
C. Salinas-Martínez de Lecea

Department of Inorganic Chemistry. University of Alicante, Ap. 99, 03080, Alicante,
Spain

Abstract

Preparation of hybrid catalysts by immobilization of the complex

$[\text{Rh}(\text{COD})\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3]^+\text{BF}_4^-$, abbreviated as Rh(NN)Si, on a wide variety of carbon materials has been investigated. The selected carbon materials, activated carbon, activated carbon fibres, activated carbon cloth, carbon nanotubes and carbon nanofibres, show very different textural properties ranging from narrow micropores to a variety of mesopore sizes. The procedure for anchorage is based on the creation of a covalent bond between the trimethoxysilane functionality in the metal complex and phenol type groups created on the surface of the carbon materials. The supports were characterized by N_2 adsorption at 77K, temperature programmed desorption (TPD) and transmission electron microscopy (TEM). The hybrid catalysts

^{*} Corresponding author. Tel: +34 96 590 3975; Fax: +34 96 590 3454 E-mail address: mcroman@ua.es

(M.C. Román-Martínez)

were characterized by X-ray photoelectron spectroscopy (XPS), X-ray absorption fine structure (XAFS), and inductively coupled plasma spectroscopy (ICP) for the determination of the metal content. The catalytic activity of the hybrid catalysts was tested in the hydrogenation of cyclohexene and carvone and it was found that they are more active than the homogeneous complex and reusable for at least 5 consecutive catalytic runs (with no leaching). Among the hybrid catalysts, those prepared with carbon nanotubes and nanofibres are noticeably more active. This behaviour has been attributed to a confinement effect due to the location of the metal complex in the hollow cavity of these supports.

Keywords : Confinement effect, carbon supports, hybrid catalysts, carbon nanotubes, hydrogenation.

1. Introduction

Immobilization of metal complexes on solid supports is a way of obtaining a novel type of catalysts that combine the advantages of homogeneous catalysts (high activity and selectivity) and the easiness of recovery of the heterogeneous catalysts. Because of this combination of properties they are usually called hybrid catalysts. Many types of supports, like silica, zeolites, clays, polymers, activated carbon, etc, have been used to immobilize metal complexes [1-4].

Carbon materials have proved to be suitable as catalyst supports, mainly due to their high versatility in textural properties, surface chemistry and morphology, as well as to their chemical stability in many conditions [5,6]. By means of oxidation treatments, surface oxygen groups can be created [7] and used to immobilize metal complexes through the formation of a covalent bond. Carboxylic groups transformed into acid

chloride groups have been successfully used to anchor different type of metal complexes [8-10]. The hybrid catalysts prepared with this method of anchorage were used in several chemical reactions. In particular, Román-Martínez et al. [10] obtained reusable catalysts for the hydroformilation of 1-octene using activated carbons as support and Baleizao et al. [9] obtained reusable carbon nanotubes based catalysts for the cyanosilylation of aldehydes. On the other hand, Mn(salen) complexes have been grafted onto activated carbon by reaction between the ligand hydroxyl groups and carbonyl and anhydride surface groups on the carbon material. These heterogeneized catalysts were tested for the epoxidation of styrene [11].

The use of phenol type groups on the surface of carbon materials for the immobilization of metal complexes has been recently reported by our group [12]. A siloxane covalent bond is created by the reaction of a trialkoxysilane functionality in a ligand and the mentioned surface oxygen groups. This type of bonding has been frequently reported for the immobilization of metal complexes on SiO₂, zeolites and silicates [13,14]. In our previous work [12], surface phenol type groups were created on activated carbons and carbon nanotubes, by a thermal treatment with air, to immobilize the rhodium complex [Rh(COD)NH₂CH₂CH₂NH(CH₂)₃Si(OCH₃)₃]⁺BF₄⁻, where COD is cyclooctadiene. The largest dimension of this rhodium complex, named Rh(NN)Si, is estimated to be about 1.5nm. It is a Rh(I) tetracoordinated complex, in which the bidentate amine ligand contains a trimethoxysilane group. Reaction of this functionality with phenol type -OH groups on the carbon surface could produce three siloxane type bonds. The catalytic properties of the heterogeneized complex were tested in the hydrogenation of cyclohexene. This is a simple test to study the catalytic activity for the C=C double

bond hydrogenation. It was found that the catalyst prepared with nanotubes was more active than the one prepared with activated carbon [12].

The present work extends the method previously reported [12] to a wider variety of carbon materials. The objective is to investigate the effect of the support textural properties on the distribution of the metal complex at the carbon surface because it could have very important consequences in the activity and selectivity of the resulting hybrid catalysts. In this work, together with the hydrogenation of cyclohexene, the hydrogenation of carvone ((R)-5-Isopropenyl-2-methyl-2-cyclohexenone) is also reported. Carvone is a terpenic monocyclic ketone, which has three different functional groups that can be hydrogenated: one C=O group, and two C=C groups (endocyclic and exocyclic). The selective hydrogenation of C=C groups produces saturated and unsaturated ketones, while the selective hydrogenation of the C=O group produces unsaturated alcohols. The reaction scheme of carvone hydrogenation can be found in the literature [15].

2. Experimental

2.1. Supports

Six carbon materials have been used as supports: A commercial activated carbon in pelletized form, named here ROX; carbon fibres from a commercial coal tar pitch, named A20; a commercial activated carbon cloth, named ACC; multi-walled carbon nanotubes (MWNTs) (named here NT) produced by the CVD method, and purified by treatment with H₂SO₄ (98%) [16] and carbon nanofibres, catalytically grown from vapour phase and purified by treatment with HCl (37%), named here GANF [17]. These

nanofibres are a heterogeneous material in which different types of structures can be found: stacked-cup nanofibres, bamboo-type cones and also fishbone nanofibres. The ash content of sample GANF is around 2.6 wt. % after the acid treatment [17].

In order to develop surface phenol type groups, the carbon materials were submitted to a heat treatment in synthetic air flow (40mL/min) for 3 hours, at 623K the activated carbon, carbon fibres, carbon cloth and carbon nanofibres, and at 773K the carbon nanotubes. The oxidized supports are identified by adding "Ox" to the name indicated above.

Additionally, the oxidized carbon nanotubes were treated in concentrated HCl aqueous solution (37%) at room temperature for 24h, to remove the catalyst used in their preparation. After this treatment, the sample was thoroughly washed with deionised water and dried (overnight at 373K). This sample is named NTOxD. The ash content was reduced from 4.0 wt.% in the original NT sample to 0.8 wt.% after the oxidation and purification treatments.

Characterization of the textural properties of the original and treated carbon materials was carried out by N₂ adsorption at 77K, using the automatic volumetric apparatus Autosorb-6B. The samples, approximately 0.1g, were previously degassed at 523K during 4 hours.

The surface chemistry of the carbon materials was analysed by means of temperature programmed desorption (TPD) experiments. Samples of approximately 5mg were heated at 20K/min up to 1300K, in a He flow of 100mL/min. The gases evolved were analysed with a mass spectrometer, Balzers MSC 200 Thermostar.

Transmission electron microscopy (TEM) analysis was performed using a JEOL JEM-2010 microscope working in the acceleration range of 100 to 200kV. The line resolution

is 0.14nm and the point resolution is 0.25nm. The microscope has coupled a microanalysis system (EDS) OXFORD Instruments, INCA Energy TEM100, with a Si(Li) detector with a resolution of 142eV.

2.2. Synthesis and characterization of the rhodium complex Rh(NN)Si

Complex Rh(NN)Si was synthesized using the following procedure. 100mg (0.520mmol) of AgBF₄ dissolved in 40mL of THF were mixed, in a round-bottom flask, with 125mg (0.252mmol) of the rhodium complex [RhCl(COD)]₂ (Aldrich) dissolved in 10mL of THF. The mixture was stirred at room temperature under an Ar atmosphere overnight to ensure the formation of complex [Rh(COD)]⁺BF₄⁻ (the coordination sphere of Rh is completed with solvent molecules). Then, the orange solution was filtered under Ar, 120μL of ligand NH₂(CH₂)₂NH(CH₂)₃Si(OCH₃)₃ (Fluka) (0.500mmol) and 10mL of CH₂Cl₂ were added and the mixture was kept under reflux for 12 hours. The orange solid formed was separated by filtration in Ar atmosphere and then, vacuum dried. Finally, a yellow solid was obtained with a yield of 70%. FTIR, ν/cm⁻¹: 3300w, 2900vs, 1650vs, 1100w, 1050w. MS m/z: 433 [M+1], 316, 222, 211, 117, 109. ¹H NMR (400MHz, in CD₃OD): δ 0.42 (t, 2H, CH₂-Si); δ 1.74 (m, 3H, NH₂CH₂, NHCH₂); δ 2.04 (m, 8H, CH₂CH=CH); δ 5.23 (m, 4H, CH=CH) δ 4.01 (q, 11H, OCH₃, CH₂-NH).

2.3. Preparation and characterization of hybrid catalysts

A solution containing 20mg of complex Rh(NN)Si in 60mL of methanol was brought in contact with 200mg of the oxidized carbon material and maintained under reflux for 16h. Afterwards, the catalysts were filtered and washed with methanol in Soxhlet for 24h. The hybrid catalysts are named adding –Rh to the name of the support.

To determine the metal content, 50mg of the catalyst were digested with 10mL H₂SO₄ (98%) and 5mL HNO₃ (65%). The suspension was heated at 573K (under reflux) until a clear solution was obtained (after about 24h). After solvent evaporation, 1mL HNO₃ (65%) and 3mL HCl (37%) were added. The obtained solution was transferred into a 10mL calibrated flask and the volume completed with deionised water. The solutions were then analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-AES), Perkin Elmer Optima 3000 and 4300.

X-ray photoelectron spectroscopy (XPS) measurements were carried out in a VG-Microtech Multilab spectrometer, using MgK α (1253.6eV) radiation from a double anode with an energy flow of 50eV. The chamber was hold at 5×10^{-10} mbar. C1s transition was adjusted at 284.6eV.

XAFS measurements were performed in Japan at the SPring-8 facility, managed by the Japan Synchrotron Research Institute (8.0 eV storage ring, station BL01B1). A Si(111) double crystal was used to monochromatize the X-ray beam from the electron storage ring. The Rh K-edge absorption spectra were recorded in the transmission mode at room temperature. The samples were packed into glass tubes. Analysis of the XAFS results was carried out using the program Athena (version 0.8.041)[18].

2.4. Catalytic activity

The hydrogenation reactions were carried out at 333K in a stainless steel Parr reactor of 40 mL volume, using 30mg of the hybrid catalyst and 10mL of a 5v/v% methanol solution of the substrate, cyclohexene or carvone. Hydrogen pressure and substrate to catalyst ratio (S:C) were, respectively, 10bar and 5000:1 for cyclohexene hydrogenation, and 20bar and 4000:1 for carvone hydrogenation. Analysis of reaction

products was performed by gas chromatography (GC), using a HP6890 Series II chromatograph, with a HP-1 Methyl Siloxane capillary column, 30m x 250 μ m x 0.25 μ m and a FID detector. To study the potential reutilization of the hybrid catalysts, after each reaction run, the catalyst was filtered in air, thoroughly washed with methanol, and then used in a new catalytic test under the same conditions. The reaction time in the first catalytic run was 30min, while in the second and consecutive runs the reaction time was 10min. Catalytic tests using the homogeneous Rh(NN)Si complex were also performed for comparison purposes. In this case, an amount of the metal complex of approximately 3mg (5.7 μ mol) was used.

3. Results

3.1. Textural properties and surface chemistry of the supports

Figure 1 shows the N₂ adsorption isotherms of the oxidized carbon materials. From a qualitative analysis of the isotherms the following information can be outlined. The isotherms obtained for the activated carbon (ROXOx), the activated carbon cloth (ACCOx) and the activated carbon fibres (A20Ox) are type I, according to the IUPAC classification [19]. The activated carbon and the activated carbon cloth are essentially microporous, the first one with a slight slope in the middle range of P/P^o and a small hysteresis loop corresponding to the presence of mesopores. The carbon fibres show the highest adsorption capacity, with a wide distribution of microporosity and some contribution of mesopores.

Isotherms of the carbon nanotubes (NTOx and NTOxD) and carbon nanofibres (GANFOx) are type IIb, generally obtained with aggregates of plate-like particles [19] and are indicative of capillary condensation. It is considered that porosity in MWNTs consists mainly of the inner hollow cores and aggregated pores formed by interaction of isolated MWNTs [20,21]. A similar consideration applies to carbon nanofibres.

However, there are some differences between these samples as the isotherm of NTOx does not show a hysteresis loop at high relative pressure. As previously reported [21,22], and according to the classical capillary condensation theory [23,24], absence of hysteresis in the N₂ isotherm of nanotubes indicates that only one end of the tube is open. Contrarily, the presence of adsorption hysteresis in the N₂ adsorption isotherms of samples NTOxD and GANFOx indicate that they contain tubes with both ends open [21,22]. The HCl treatment carried out to the oxidized nanotubes removes a large part of the metal particles (catalyst for nanotube growth), that are usually located at the tube end. Because of that, the tubes can be opened in both ends. In the case of the nanofibers, the preparation conditions, including the purification treatment with HCl can lead, as previously reported [17], to some structures with a hollow core and two ends opened.

To corroborate the presence of opened tubular structures, a TEM analysis of the carbon nanotubes and carbon nanofibres has been carried out. The results are presented below. The calculated BET surface area, mesopore volume, external area and average pore size are presented in Table 1. The volume of mesopores with $2\text{nm} < \phi < 20\text{nm}$ was calculated by the difference between the volume of N₂ adsorbed at $P/P^0=0.9$ and $P/P^0=0.2$ (expressed as liquid). The external surface S_{ext} (excluding the area corresponding to micropores), was calculated by the de Boer's t-method [19,24]. The average pore size was obtained using the Gurvich rule [24]. Assuming that no surface

exists other than the inner walls of the pores, and that the pores are of cylindrical geometry, the average pore radius can be calculated from the ratio of the total pore volume (at $P/P^0=0.95$) and the BET surface area [24].

BET surface areas correspond to the expected values for activated carbon materials and carbon nanotubes and nanofibres. With the exception of sample ACCOx, the supports have a relatively high mesopore volume. In the case of nanotubes and nanofibres, S_{ext} is close to S_{BET} , as it is in materials with low or no microporosity. On the other hand, materials like the activated carbon fibres (A20Ox) or the activated carbon cloth (ACCOx) show a very small external surface area because their surface is mainly associated to micropores. Even though the model used to calculate average pore size is not very adequate for activated carbons, carbon fibres and activated carbon cloth because the pores are not cylindrical but slit-shaped, it can give an idea of the differences in pore size in these materials. The average pore size of the supports show that for carbon nanotubes and carbon nanofibres it is in the range of mesopores while for activated carbons (ROXOx, A20Ox, ACCOx) the average is in the micropore range. Figures 2A and 2B show TEM images of samples NTOx and NTOxD, respectively. The structure of the multiwalled carbon nanotubes is clearly observed. It must be pointed out that these nanotubes are quite long. In the case of sample NTOx (Figure 2A) the metal particle at one end of the nanotube is observed. After the purification treatment (sample NTOxD, Figure 2B) most of the nanotubes show both ends opened. The internal diameter observed in the micrographs varies from 6 to 9 nm in agreement with the average pore diameter obtained from adsorption results.

Figure 3 shows a TEM image of the carbon nanofibres GANFOx. As already mentioned, it can be observed that they are a heterogeneous material but there is an

important amount of opened tubular structures, with diameters of the inner cavity in a wide range, from 5 to 60nm.

Amounts of CO and CO₂ evolved in TPD experiments are shown in Table 2 (expressed as μmol per gram of support). The corresponding total amount of oxygen has been calculated (as weight percentage) and included. The values reported in Table 2 considerably differ among samples and are indicative, in all cases, of a significant surface oxidation. As mentioned in the introduction, the aim of this work is to use –OH phenol functionalities to produce siloxane-type bonds with the metal complex.

Considering that phenol groups decompose as CO between 873 and 973K [25], a deconvolution analysis of the CO desorption profile has been used to estimate the amount of this type of functionalities (also included in Table 2). With the exception of sample A20Ox, the amount of phenol type groups is similar in all the supports.

However, considering the important differences in surface area, the concentration of phenol groups at the surface should be appreciably different. The ratio between the number of –OH phenol type groups per gram of support and the surface area of the support (in nm^2/g) has been calculated in order to have an idea of the concentration of these groups. The results, expressed as –OH groups per 10 nm^2 , are included in Table 2. Assuming that the distribution of –OH groups is homogeneous all over the support surface, these data indicate that in carbon nanotubes and nanofibres –OH groups are relatively close, while the concentration is much lower in the activated carbon materials.

The reaction of the trialkoxysilane functionality in the diamine ligand of complex Rh(NN)Si with three phenol groups on the carbon surface producing three siloxane-type bonds requires a short distance between them.

3.2. Characterization of hybrid catalysts

Table 3 shows the results of the XPS analysis carried out on the hybrid catalysts. The binding energy found for Rh3d_{5/2} corresponds to Rh(I) and nitrogen appears mainly as amine nitrogen (N_a) (BE= 400.7eV). The ratio N_a/Rh found is close to 2, in agreement with the nature of the Rh(NN)Si complex. In the case of catalyst NTOx-D-Rh, signals for Rh or N were not observed. Since the sample contains Rh, as will be shown later on, the complex must be located in the inner cavity of the nanotube, and cannot be detected because the depth of analysis of this technique is about 2nm. The atomic ratio Rh/C considerably differs for the different catalysts. This is a consequence of the different content and distribution of Rh on the support surface.

XAFS analysis has been used to study possible changes in the state of complex Rh(NN)Si after immobilization. XAFS measurements have been done with the unsupported complex (as a solid) and with the complex supported on the activated carbon and on the carbon nanotubes. The X-ray absorption near-edge spectra of these samples are shown in Figure 4. By comparison of the spectra of Rh(NN)Si and ROXOx-Rh and NTOx-Rh, information can be obtained about any modification of the oxidation state of rhodium. The absorption edge in both supported catalysts is almost identical to that of the unsupported Rh(NN)Si. Thus, it can be concluded that in the supported complex, rhodium remains in the monovalent oxidation state in agreement with the XPS analysis. Figure 5 shows the experimental EXAFS data of the three samples analysed. The high similarity between the spectra of the unsupported complex and samples ROXOx-Rh and NTOx-Rh reveals that the coordination of Rh in the complex has not been modified upon heterogenization. Besides, it must be mentioned that the low EXAFS intensity at larger values of k ($k > 10\text{\AA}^{-1}$) indicates the absence of

high Z scatterers, that is, it can be concluded that no Rh-Rh interactions are present. In summary, this qualitative analysis of the XAFS data supports the idea that the environment of Rh in the complex Rh(NN)Si is the same in the supported and unsupported states of this molecule.

The maximum Rh content in the hybrid catalysts (considering the amounts of complex and support used) can be 2 wt.%. However, the actual rhodium content of the catalysts, shown in Table 4, is quite far from that value. As stated in the experimental section, the catalysts were washed with methanol after impregnation in order to remove loosely adsorbed species. So, the differences in the amount of Rh loaded must be related to both, the amount and accessibility of anchorage sites on the different supports. If the amount of –OH phenol groups (4th data column in Table 2) is compared to the Rh content in $\mu\text{mol/g}$ (2nd data column in Table 4), a ratio of 3 or higher is obtained for all the samples, except for ACCOx-Rh, meaning that the proposed bonding through three siloxane type bonds is possible if the –OH groups are accessible and close enough.

3.3. Cyclohexene hydrogenation

3.3.1. Catalytic behaviour of the hybrid catalysts

Table 5 shows the catalytic activity for cyclohexene hydrogenation (after 30min reaction time), expressed as turnover frequency (in s^{-1}), for the unsupported complex Rh(NN)Si and the hybrid catalysts. The number of active sites is determined from the rhodium content (fresh samples) shown in Table 4, considering that each atom of Rh is forming an active and accessible complex.

With the exception of sample A20Ox-Rh, the hybrid catalysts are more active than the homogeneous complex, and, among them, very different TOFs are observed. It seems that the textural properties of the supports have an important effect. It is striking the high activity of catalyst NTOxD-Rh. Also, the inactivity of catalyst A20Ox-Rh, in spite of having the highest Rh content, is an unexpected result.

Table 6 shows the catalytic activity in five consecutive runs. Excepting sample A20Ox-Rh, which remains inactive, in a second catalytic run all the catalysts show an increase of catalytic activity. This means that the Rh complex remains anchored, at least partially, and probably has suffered some modifications under reaction conditions that produce more active species. The activity in three more consecutive catalytic runs is similar to that in the second one, that is, deactivation was not observed. Activity is calculated as mol of cyclohexene converted per mol of Rh present in the fresh catalysts per second. It is, obviously, not a real TOF because the actual amount of Rh in each run is not known, but it is a useful way to compare the activity in consecutive runs.

3.3.2. *Study of used catalysts*

The Rh content in the used catalysts after the first and the fifth catalytic run is shown in Table 4. It can be observed that the complex is almost not leached from catalysts ROXOx-Rh, GANFOx-Rh, NTOx-Rh and NTOxD-Rh, but it is leached, although in different extent, from ACCOx-Rh and A20Ox-Rh. These results indicate that the anchorage of the Rh complex on the support surface is different in these two groups of hybrid catalysts.

Results of the XPS analysis of the used catalysts (after five consecutive catalytic runs) are presented in Table 7. These data show that in the used catalysts ROXOx-Rh,

A20Ox-Rh, NTOx-Rh and GANFOx-Rh, neither the B.E. of Rh nor the N_a/Rh ratio have changed. As in the case of the fresh catalyst, XPS signals of Rh and N are not observed for sample NTOxD-Rh. In catalyst ACCOx-Rh two different states of rhodium are found: at 309.7eV and at 307.8eV, which correspond to Rh(I) and Rh(0), respectively. These XPS data indicate that, with the exception of sample ACCOx-Rh, the complex is not electronically modified under reaction conditions and the coordination with amines is not lost. The atomic ratio Rh/C decreases for catalysts ACCOx-Rh and A20Ox-Rh, in accordance to the observed complex leaching.

3.4. Carvone hydrogenation

Samples NTOxD-Rh and GANFOx-Rh, the most active catalysts in the previous test, and sample ROXOx-Rh, for comparative purposes, have been tested as catalysts for the hydrogenation of carvone. Figure 6 shows carvone conversion to different products versus time. Observed products are carvotanacetone, carvomenthone and the hemiacetal of carvomenthone, produced by the interaction of the substrate with the solvent (methanol). The sequence of reactions is presented in Figure 7. A previous catalytic test with the homogeneous Rh(NN)Si showed that the activity of this complex is very low: carvone conversion was only 6% after 24 hours. The product obtained was mainly carvotanacetone, with some conversion to carvomenthone.

It can be observed that with catalysts NTOxD-Rh and GANFOx-Rh complete conversion of carvone is achieved after about 15 and 40 minutes, respectively, while at similar reaction time, catalyst ROXOx-Rh shows a very low catalytic activity. These results reveal a very important effect of the textural properties of the support in the catalytic activity of the heterogenized complex.

Catalyst NTOxD-Rh is very active for the hydrogenation of double bonds C=C, mainly producing the saturated ketone. Carvotanacetone obtained in the first hydrogenation step is rapidly converted to carvomenthone, so that after 40 minutes it is completely consumed. The interaction of the carbonyl group of this molecule with methanol takes place to form the hemiacetal, which appears in a relatively high concentration after 1 hour reaction time. TOF value for this catalyst is 5.38s^{-1} (calculated at 15min of reaction).

Contrarily, catalyst GANFOx-Rh shows a high selectivity to the unsaturated ketone. It shows a slower kinetics, particularly in the hydrogenation of carvotanacetone to carvomenthone. At a total conversion of carvone (40 minutes) the selectivity to carvotanacetone is 90% being the other product carvomenthone. TOF value obtained at 40min reaction time is 1.81s^{-1} . Reutilization tests carried out with this catalyst show good activity and stability after 4 consecutive runs without changing the selectivity to carvotanacetone.

The Rh content in the used catalysts was similar to that of the fresh catalysts as observed for cyclohexene hydrogenation.

4. Discussion

4.1. Rh complex distribution on the carbon surface

In the case of catalysts prepared with the activated carbon, activated carbon cloth and carbon fibres, the Rh content of fresh samples (Table 4) could be related to the support BET surface area (Table 1) and the amount of -OH phenol groups (Table 2). The highest Rh loading of catalyst A20Ox-Rh corresponds to the highest values of BET surface area and amount of -OH phenol groups. However, that relation does not apply for carbon nanotubes and nanofibres. Other correlations with textural properties or

oxygen surface groups are also failed. At the moment, no clear explanation has been found for the different values obtained, regarding the differences in textural and chemical properties of the supports. As mentioned before, the differences in the amount of Rh loaded must be related to the amount and accessibility of anchorage sites on the different supports. Anchorage sites for the desired bonding are -OH phenol groups, however, the possibility of other kind of interactions, with other oxygen groups cannot be ruled out.

The calculated Rh/C ratio from XPS analysis (Table 3) can give an idea about the location of the complex in the carbon porosity. Considering a total ratio Rh/C estimated from the amount of Rh in each catalyst (Table 4), the factor $F = \text{Rh/C(XPS)}/\text{Rh/C(total)}$ has been calculated and included in Table 3. A higher value of factor F means a more external location. It can be deduced that in the activated carbon and, particularly, in the activated carbon cloth, the complex is more externally located than in the other supports. The low F value obtained for sample A20Ox-Rh is an indication of the internal location of the complex. It should be noted the inverse relation between F and V_{meso} (Table 1). These results indicate that the Rh complex can be located in the mesopores of the supports but not in the micropores which is consistent with the size of the complex (1.5 nm in the largest dimension). In addition, the rhodium complex is more likely located in the hollow cavity of NTOxD nanotubes because, as concluded from the N_2 adsorption isotherm, in this sample the nanotubes have both ends opened and this favours the entering of the complex containing solution, due to capillarity and flow phenomena [23,24]. In the case of the support GANFOx, because of its heterogeneity, part of the complex must be in the inner space of the tubular structures and part of it on an external location.

It must be noted here that in the case of the supports with a surface area associated mainly to micropores, the accessibility of the complex to surface phenol groups is probably quite limited. As already mentioned, in the case of the activated carbon, carbon cloth and carbon fibres, the phenol groups are located distant from each other (Table 2), so the desired three -OH groups may be too far away to produce an effective anchorage. In the case of the carbon nanotubes and nanofibres, the higher concentration of phenol groups indicates that the phenol groups at the surface are closer and so the rhodium complex could be more effectively anchored in these cases.

These results indicate that on supports NTOx, NTOxD and GANFOx, the anchorage can mainly occur by the formation of three siloxane bonds, while in the case of supports ROXOx, ACCOx and A20Ox the anchorage must take place by the formation of one or two siloxane bonds. Besides, in the case of ACCOx and A20Ox an important part of the complex could be anchored by physical adsorption. This would explain the progressive leaching of the metal complex from the supports ACCOx and A20Ox in consecutive catalytic runs, while it remains almost unchanged in the other supports.

Factor **F** was also calculated, as indicated above, for the catalysts used in 5 catalytic runs. The values are included in Table 7. This parameter indicates that the relative location of the complex does not significantly change upon catalysts use. Only in the case of sample ACCOx-Rh it seems that the proportion of external Rh has increased.

4.2. Effect of support textural properties on the catalytic activity for cyclohexene hydrogenation

To analyze the effect of the textural properties of the supports in the catalytic activity, TOF values obtained in the first catalytic run have been plotted against S_{BET} , S_{ext} , and

mesopore volume. Only in the case of the external surface area (as defined above), an almost linear positive relationship is found (Figure 8), but in which the activity of catalyst NTOxD-Rh is clearly out of the trend.

It is interesting to compare the results obtained with samples NTOx-Rh and NTOxD-Rh. The two supports, NTOx and NTOxD, have similar textural properties (S_{BET} , S_{ext} , etc.), but as indicated before, the purified nanotubes seem to have the two ends opened, while in sample NTOx one end might be closed by the metal particle used for the nanotube growth. As mentioned above, the Rh complex in NTOxD-Rh is likely located in the inner hollow cavity of the nanotubes. This is so because a liquid can more easily enter tubes which are opened on both ends. Capillarity and flow phenomena considerations can also be important when considering the access of reactants to the active sites. Besides, inside the tube there is a confinement of reactants close to the active sites [26,27]. These two facts could explain the higher activity of sample NTOxD-Rh over sample NTOx.

The behaviour of catalyst GANFOx-Rh can also be explained with the comments indicated above, but taking into account that these nanofibres are a very heterogeneous material in which only a fraction consists of two-end open tubes, as explained before [17].

The case of catalyst A20Ox-Rh is also striking as it is inactive although a relatively large part of the complex remains anchored and the XPS results do not reveal important modifications upon anchoring and use. In this case we deduce from the low F value that the chemically anchored complex is located inside the porosity of this carbon material, in small mesopores, where the place for the coordination of the substrate is quite limited, and because of that there is no catalytic activity. In the case of the activated

carbon cloth, ACCOx, the main problem seems to be the weak anchorage of the complex on the support as it is extensively leached, already after the first catalytic run (Table 4). The active species is the complex either anchored, probably on the very low external surface (Table 1), or in solution after leaching, and because of that the catalytic activity of sample ACCOx-Rh is very similar to that on the unsupported complex (Table 5). The reason should be the lower ratio –OH groups/Rh previously commented (section 3.2). Although the complex is gradually lost in consecutive runs, the activity does not decrease and this can be related to the modification of the electronic state of Rh determined by XPS (part of it is reduced, see Table 7).

Catalyst ROXOx-Rh shows a good activity in the cyclohexene hydrogenation despite having a structure mainly microporous. This behaviour could be explained by the presence in support ROXOx of a significant amount of small mesopores leading to a considerable S_{ext} (109 m²/g). Moreover, the average pore size of this sample is slightly larger than those of supports A20Ox and ACCOx, as shown in Table 1. This support produces a catalyst that, although less active than those prepared with the nanotubes and nanofibres, is much more active than the homogeneous complex and very stable.

From these results it can be concluded that the catalytic activity for cyclohexene hydrogenation seems to be enhanced by the location of the metal complex inside the porosity in a way in which the reactants can be confined close to the active site. It is also necessary that there is place enough for the processes of coordination, transformation and dissociation of the product that constitute the catalytic cycle. The better results obtained with nanotubes and nanofibres indicate that the tubular structure with two ends opened is quite beneficial. Figure 9 illustrates the proposed scheme of the metal complex anchored on the inner cavity of a tubular structure.

4.3. Effect of support textural properties on the activity and selectivity in carvone hydrogenation

As concluded from the results of cyclohexene hydrogenation, the metal complex is more active when located inside the porous network, with a minimum pore diameter. Compared to cyclohexene, the carvone molecule is more voluminous and probably the activity of catalyst ROXOx-Rh is so low (Figure 6) because most of the pores are too small (the average pore size of this support is 1.20nm).

The different activity and selectivity of catalysts NTOxD-Rh and GANFOx-Rh could be explained considering both, the proportion of structures with a hollow core, and the diameter of this core in each support. Support NTOxD is almost entirely constituted by MWNT with a quite homogeneous inner diameter (that averages 9.8 nm from adsorption measurements or 6-9 nm from TEM). On the contrary, support GANFOx contains different type of nanofibres (with and without a hollow core) and also some non structured material. On the other hand, the open hollow nanofibres show a very broad distribution of diameter sizes (from 5 to over 60 nm from TEM).

As deduced from the results on cyclohexene hydrogenation, the two ends open feature of these tubular supports seems to be very important for an appropriate location of the metal complex, which is responsible of a high activity (justified by the above mentioned confinement and flow and capillarity effects). The diameter of the tube must also play an outstanding role as the more heterogeneous catalyst GANFOx-Rh is less active than NTOxD-Rh. In the case of carvone hydrogenation, this has, as well, a very important consequence in selectivity. Catalyst GANFOx-Rh has a high selectivity to the

unsaturated ketone while the more active catalyst NTOxD-Rh produces the saturated ketone.

The product distribution shown by sample NTOxD-Rh is similar to the one previously reported by Mastrorilli et al. [28] using a Rh β -ketoesterate complex immobilized on a cross-linked polymer. Reaction conditions were atmospheric pressure, room temperature and a S/C ratio of 160 and thus, the total conversion of carvone was achieved after 6.5 hours. The authors indicate that complex leaching was not observed, but data on reutilization are not reported.

Carvone hydrogenation has been usually carried out with heterogeneous supported mono- and bimetallic catalysts. Table 8 shows a summary of some literature data as well as the results of this work. It can be seen that in the case of the heterogeneous catalysts, the values of selectivity to carvotanacetone are good, but the reaction times are too long, while with our catalysts, comparable and better results of selectivity are obtained in less than 1 hour reaction. Also, the catalysts NTOxD-Rh shows a high selectivity (> 90%) towards carvomenthone after 35 minutes of reaction, while other catalysts only have a maximum of 40% of selectivity and after longer periods.

After this summary of results obtained with other types of catalysts it can be concluded that catalysts NTOxD-Rh and GANFOx-Rh are suitable for carvone hydrogenation as they are very active and selective to ketones.

5. Conclusions

Different carbon materials have been used to immobilize a Rh diamine complex, obtaining hybrid catalysts. The Rh complex was effectively anchored on the carbon surface without significant alterations. The hybrid catalysts are more active than the

homogeneous complex in the hydrogenation of cyclohexene when the active species is located inside the support porosity of adequate size. In general, a support with high surface area in pores larger than micropores appears to be the most appropriate for this application. A minimum diameter of pores is required for the confinement of the metal complex and the accessibility of the reactants, and the tubular structure with two ends opened present in samples NTOxD-Rh and GANFOx-Rh leads to the best catalytic results. The hybrid catalysts obtained with the nanotubes, nanofibres and activated carbon are stable and recyclable. The geometrical requirements indicated above are more patent if a voluminous substrate must be hydrogenated. Thus, for carvone hydrogenation the active species must be located in pores of several nanometres, that is the case of catalysts NTOxD-Rh and GANFOx-Rh. Differences in selectivity of these two samples are considered to be related with the different inner diameters of the tubular supports, being the reaction faster in catalyst NTOxD-Rh, but more selective in GANFOx-Rh.

Acknowledgements: The authors would like to thank the financial support to the Spanish Government, Project CTQ2005-01358/PPQ, the Generalitat Valenciana, Project GV06/116 and Japan Synchrotron Research Institute JASRI for beam time allocation at SPring-8, through project 2006A1127. L.J. Lemus-Yegres also thanks the University of Alicante for her research grant. Dr. P. Serp is sincerely acknowledged for providing sample NTOx and valuable information about it. Grupo Antolín Ingeniería S.A. is acknowledged for providing sample GANF.

6. References

- [1] Y. I. Yermakov, B.N. Kuznetsov, V.A. Zakharov. *Studies in Surface Science and Catalysis*, Elsevier, 1981 Vol. 8.
- [2] B.E. Hanson in: R. Bruce King, E. Board (Eds.), *Enc. Inorg. Chem.* John Wiley and Sons. (1994), London, Vol. 7, p. 4056.
- [3] W. Keim, B. Drißben-Hölscher in: G.Ertl, H. Knözinger, J. Weitkamp (Eds.), *Heterogenization of Complexes and Enzymes. Handbook of Heterogeneous Catalysis*, VCH, Weinheim, 1997, Vol. 1.
- [4] I.F.J. Vankelecom, P.A. Jacobs in: D. De Vos, I. Vankelecom, P. Jacobs (Eds.), *Chiral catalyst immobilization and recycling*, Wiley-VCH, Verlag, 2000, Ch. 2.
- [5] L. Radovic, F. Rodríguez-Reinoso, *Chemistry and Physics of Carbon*, Dekker, 1997, Vol. 25, Ch.1, p.243.
- [6] E. Auer, A. Freund, J. Pietsch, T. Tacke, *Appl. Catal. A* 173 (1998) 259.
- [7] Y.Otake, R.G. Jenkins, *Carbon* 31 (1993) 109.
- [8] A. Silva, M. Martins, M. Freitas, A. Valente, C. Freire, B. Castro, J. Figueiredo, *Microporous Mesoporous Mater.* 55 (2002) 275.
- [9] C. Baleizao, B. Gigante, H. García, A. Corma, *J. Catal.* 221 (2004) 77.
- [10] M. Román-Martínez, J. Díaz-Auñón, C. Salinas-Martínez de Lecea, H. Alper, J. *Molec. Catal. A: Chem.* 213 (2004) 177.
- [11] A. Silva, J. Figueiredo, C. Freire, B. Castro, *Microporous Mesoporous Mater.* 68 (2004) 83.
- [12] L. Lemus-Yegres, I. Such-Basáñez, C. Salinas-Martínez de Lecea, P. Serp, M. C. Román-Martínez, *Carbon* 44 (2006) 605.

- [13] H. Gao, R. Angelici, *New J. Chem.* 23 (1999) 633.
- [14] M. Alcón, A. Corma, M. Iglesias, F. Sánchez, *J. Organomet. Chem.* 655 (2002) 134.
- [15] S. De Miguel, M.C. Román Martínez, D. Cazorla-Amorós, E. Jablonski, O. Scelza, *Catal. Today* 66 (2001) 289.
- [16] M. Corrias, B. Caussat, A. Ayral, J. Durand, Y. Kihn, P. Kalck, P. Serp, *Chem. Eng. Sci.* 58 (2003) 4475.
- [17] I. Martín-Gullón, J. Vera, J. Conesa, J. González, C. Merino, *Carbon* 44 (8) (2006) 1572.
- [18] B. Ravel, M. Newville, *J. Synchrotron Rad.* 12 (2005) 537.
- [19] F. Rouquerol, J. Rouquerol, K. Sing, *Adsorption by powders and Porous Solids*, Academia Press, 1999.
- [20] Q. Yang, P. Hou, S. Bai, M. Wang, H. Cheng, *Chem. Phys. Lett.* 345 (2001) 18.
- [21] S. Inoue, N. Ichikuni, T. Suzuki, T. Uematsu, K. Kaneko, *J. Phys. Chem. B* 102 (1998) 4689.
- [22] J. Broekhoff, B. Linsen, in: B.G. Linsen (Ed.), *Physical and chemical aspects of adsorbents and catalysis*, Academic Press, 1970, Ch. 1.
- [23] S. Gregg, K. Sing, *Adsorption, surface area and porosity*, Academic Press, 1982.
- [24] S. Lowell, J. Shields, M. Thomas, M. Thommes, *Characterization of Porous Solids and Powders: Surface area, pore size and density*, Kluwer Academy Publishers, 2004.
- [25] J. Figueiredo, M. Pereira, M. Freitas, J. Orfao, *Carbon* 37 (1999) 1379.
- [26] Y. Zhang, H. Zhang, G. Lin, P. Chen, Y. Yuan, K. Tsai, *Appl. Catal. A* 187 (1999) 213.

- [27] S. Pariente, P. Trens, M.F. Fajula, F. Di Renzo, N. Tanchoux, *Appl. Catal. A*. 307 (2006) 51.
- [28] P. Mastrorilli, A. Rizzuti, G. Suranna, C. Nobile, *Inorg. Chim. Acta* 304 (2000) 17.
- [29] R. Meléndrez, G. Del Angel, V. Bertin, M. Valenzuela, J. Barbier, *J. Molec. Catal. A: Chem.* 157 (2000) 143.
- [30] G. Del Angel, R. Meléndrez, V. Bertín, J. Domínguez, P. Marecot, J. Barbier in: M.E.A. Guisnet (Ed.), *Heterogeneous Catalysts and Fine Chemicals III*, 1993, p. 171.
- [31] G. Torres, S. Ledesma, E. Jablonski, S. De Miguel, O. Scelza, *Catal. Today* 48 (1999) 65.
- [32] S. De Miguel, M.C. Román-Martínez, E. Jablonski, J. Fierro, D. Cazorla-Amorós, O. Scelza, *J. Catal.* 184 (1999) 514.

Figure Captions

Figure 1. Adsorption isotherms of N₂ at 77K.

Figure 2. TEM image of (A) the oxidized NTOx and (B) oxidized and purified carbon nanotubes NTOxD

Figure 3. TEM images of the oxidized carbon nanofibers GANFOx

Figure 4. XANES spectra of complex Rh(NN)Si and of hybrid catalysts

Figure 5. EXAFS spectra of complex Rh(NN)Si and of hybrid catalysts

Figure 6. Product distribution versus time in carvone hydrogenation with catalysts NTOxD-Rh, GANFOx-Rh and ROXOx-Rh

Figure 7. Reaction scheme of carvone hydrogenation

Figure 8. Activity of hybrid catalysts in cyclohexene hydrogenation versus supports external surface area (S_{Ext})

Figure 9. Scheme of the location of the metal complex on the hollow cavity in catalyst NTOxD-Rh

Table 1. BET surface area, mesopore volume and average pore size of the oxidized supports

Sample	S_{BET} (m^2/g)	$V_{\text{meso}}^{(a)}$ (cm^3/g)	$S_{\text{ext}}^{(b)}$ (m^2/g)	Average pore size ^(c) (nm)
ROXOx	1028	0.12	109	1.2
ACCOx	1422	0.02	6	0.8
A20Ox	2004	0.19	36	1.0
NTOx	224	0.22	207	9.7
NTOxD	228	0.22	212	9.8
GANFOx	180	0.17	167	7.6

(a) Volume of mesopores, calculated subtracting the volume at $P/P^0=0.9$ and the volume at $P/P^0=0.2$, pores with $2\text{nm} < \phi < 20\text{nm}$

(b) External surface area, calculated from t-method values [19,24]

(c) Calculated from Gurvich rule [24]

Table 2. CO and CO₂ evolved in a Temperature Programmed Desorption experiment up to 1300K, total oxygen, and amount and concentration of –OH phenol groups

Sample	CO ($\mu\text{mol/g}$)	CO ₂ ($\mu\text{mol/g}$)	O (wt.%)	-OH phenol ^a ($\mu\text{mol/g}$)	-OH groups per 10nm^2
ROXOx	1750	510	4.4	170	1
ACCOx	1570	1010	5.7	149	0.63
A20Ox	3600	1210	9.6	432	1.25
NTOx	630	330	2.1	177	5
NTOxD	580	150	1.4	177	5
GANFOx	1450	330	3.4	208	10

^a Calculated by deconvolution analysis of the CO desorption profile

Table 3. XPS data of the fresh hybrid catalysts

Sample	Rh3d _{5/2} B.E.(eV)	N1s B.E.(eV)	N _a /Rh	Rh/C	F ^(a)
ROXOx-Rh	309.6	400.7	1.6	0.0063	9.9
ACCOx-Rh	309.6	400.7	2.6	0.0150	17.4
A20Ox-Rh	309.6	400.4	2.5	0.0053	3.5
NTOx-Rh	309.8	400.9	1.8	0.0035	4.6
NTOxD-Rh	n.d.	n.d.	--	--	--
GANFOx-Rh	309.7	400.6	2.0	0.0023	5.3

(a) F is calculated dividing the atomic ratio Rh/C obtained from XPS by the atomic total ratio Rh/C

Table 4. Rhodium content in the hybrid catalysts, fresh and after having been used for cyclohexene hydrogenation, and % of complex leached after 5 catalytic runs

Sample	Rh	fresh	Rh after 1 run	Rh after 5 runs	% Leaching after 5 runs
	wt. %	$\mu\text{mol/g}$	$\mu\text{mol/g}$	$\mu\text{mol/g}$	
ROXOx-Rh	0.54	53	52	52	3.7
ACCOx-Rh	0.74	72	57	13	83.5
A20Ox-Rh	1.30	126	88	86	33.6
NTOx-Rh	0.65	63	63	61	1.6
NTOxD-Rh	0.28	27	27	27	1.8
GANFOx-Rh	0.37	36	35	35	1.8

Table 5. TOF in cyclohexene hydrogenation of the homogeneous complex and the hybrid catalysts (calculated after 30 minutes reaction time)

Sample	TOF (s^{-1})
Rh(NN)Si	0.08
ROXOx-Rh	1.89
ACCOx-Rh	0.31
A20Ox-Rh	0.001
NTOx-Rh	2.06
NTOxD-Rh	4.44
GANFOx-Rh	2.48

Table 6. Activity values (s^{-1}) of the hybrid catalysts in consecutive catalytic runs of cyclohexene hydrogenation.

Cycle	ROXOx-Rh	ACCOx-Rh	NTOx-Rh	NTOxD-Rh	GANFOx-Rh
1	1.89	0.31	2.06	4.44	2.48
2	1.91	0.43	4.54	10.83	6.69
3	2.03	0.41	4.24	10.94	7.17
4	2.01	0.43	4.28	11.89	6.92
5	2.22	0.40	3.91	11.89	6.92

Table 7. XPS data of the used hybrid catalysts (after 5 consecutive catalytic runs in cyclohexene hydrogenation)

Sample	Rh3d _{5/2} B.E.(eV)	N1s B.E.(eV)	N _a /Rh	Rh/C	F ^(a)
ROXO _x -Rh	309.7	400.6	1.7	0.0061	9.8
ACCO _x -Rh	309.7 (56.9%) 307.8 (43.1%)	400.6	2.5	0.0070*	47.4
A20O _x -Rh	309.5	400.5	2.4	0.0031	3.0
NTO _x -Rh	309.6	400.8	1.8	0.0034	4.6
NTO _x D-Rh	n.d.	n.d.	--	--	--
GANFO _x -Rh	309.6	400.7	1.9	0.0021	5.0

* Calculated with the amount of Rh (I) present in the sample.

(a) F is calculated dividing the atomic ratio Rh/C obtained from XPS by the atomic total ratio Rh/C

Table 8. Summary of carvone hydrogenation results from the literature. Data of the present work are included

Catalyst	T (K)	P (bar)	TOF (s ⁻¹)	% Carvotanacetone	% Carvomenthone	Ref.
Rh complex-polymer	294	1	0.69*10 ⁻²	77	---	28
Pd/SiO ₂	373	20	0.07	70	30	29
Pd-Cu/SiO ₂	373	20	0.58	60	40	30
PtSn/Al ₂ O ₃	363	20	0.83*10 ⁻²	65	10 ^(a)	31
PtSn/C	313	1	0.50*10 ⁻⁴	80	--- ^(b)	15,
Pt/C			0.92*10 ⁻³	96	1 ^(c)	32
NTO _x D-Rh	333	20	5.38	60	40 ^(d)	This work
GANFO _x -Rh	333	20	1.81	90	10	This work

(a) About 25% saturated alcohol obtained.

(b) About 20% of unsaturated alcohol was obtained in this sample.

(c) About 2% of unsaturated alcohol obtained.

(d) After 35 minutes of reaction the selectivity to carvomenthone was of 90%

Figure 1. Adsorption isotherms of N_2 at 77K.

Figure 2. TEM image of (A) the oxidized NTOx and (B) oxidized and purified carbon nanotubes NTOxD

Figure 3. TEM images of the oxidized carbon nanofibers GANFOx

Figure 4. XANES spectra of complex Rh(NN)Si and of hybrid catalysts

Figure 5. EXAFS spectra of complex Rh(NN)Si and of hybrid catalysts

Figure 6. Product distribution versus time in carvone hydrogenation with catalysts NTOxD-Rh, GANFOx-Rh and ROXOx-Rh

Figure 7. Reaction scheme of carvone hydrogenation

Figure 8. Activity of hybrid catalysts in cyclohexene hydrogenation versus supports external surface area (S_{Ext})

Figure 9. Scheme of the location of the metal complex on the hollow cavity in catalyst NTOxD-Rh