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Immobilised chiral inducer on Pt-based mesoporous titanate nanotubes as heterogeneous catalysts for enantioselective hydrogenation

Cristian H. Campos^a, Cecilia C. Torres^a, Paula Osorio-Vargas^b, Claudio Mella^b, Julio

Belmar^a, Doris Ruiz^b, José L.G. Fierro^c, Patricio Reyes^b

^aDepartamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad de Concepción, Edmundo Larenas 129 Concepción, Chile

^bDepartamento de Fisicoquímica, Facultad de Ciencias Químicas, Universidad de Concepción, Edmundo Larenas 129 Concepción, Chile

^cInstituto de Catálisis y Petroleoquímica, CSIC, Marie Curie 2, Cantoblanco 28049, Madrid, Spain

*ccampos@udec.cl

ABSTRACT

A new series of chiral porous titanate nanotubes (TNTs) containing (–)-11-trimethoxysilylcinchonidine (TMS-CD) moieties were synthesized via direct surface anchorage. These hybrid solids were used as supports for Pt (1%wt) catalysts and evaluated in heterogeneous enantioselective hydrogenation of 1-phenyl-1,2-propanodione. The supports and catalysts were characterized by a variety of techniques including TGA, N₂ adsorption isotherms, solid state NMR (¹³C and ²⁹Si), XRD, HR-TEM, DRIFTs, and XPS. For the best system the hydrogen pressure, solvent effects and recycles were studied. The maximum enantiomeric excess (ee) and the turnover frequency obtained under optimized

conditions with 1%Pt/TNT-CD were 37% (at 15%wt nominal content of TMS-CD) and 165 min^{-1} (at 10%wt nominal content of TMS-CD), respectively. The variation of H₂ pressure and solvent affects both the activity and enantioselectivity due to the substrate adsorption on the metal active sites. Additionally, these heterogeneous catalysts can also be easily recycled and reused for three times without the loss of activity and enantioselectivity. After the 3th cycle, catalyst deactivation due to the leaching of Pt nanoparticles and modifier hydrogenation in the feed was detected.

KEYWORDS: Titanate nanotubes catalysts; chiral supports; 1-phenyl-propane-1,2-dione; enantioselective hydrogenation.

1. INTRODUCTION

The enantioselective hydrogenation of α -keto esters in the presence of platinum modified by cinchona alkaloids was first reported by Orito et al. in 1979 [1] and has been the subject of extensive studies particularly in recent years [2-4]. One of the few heterogeneous catalytic systems identified for asymmetric hydrogenation with synthetically useful enantioselectivities is the cinchona-modified Pt/y-Al₂O₃ for hydrogenation of α -diketones, which was first reported by Vermeer *et al.* in 1993 [5]. Due to the conjugated keto groups of the reactant, the hydrogenation proceeds in two consecutive steps. 1-Phenyl-1,2-propanedione (PPD) is a suitable molecule to investigate the enantioselective hydrogenation of conjugated carbonyl bonds [3, 6-11]. It contains a phenyl ring and two carbonyl groups. Under the reaction conditions, in the presence of (-)cinchonidine (CD), the main product is (R)-1-hydroxy-1-phenylpropanone (1R-FP), an important intermediate in the synthesis of some drugs [12]. Nevertheless, reaction conditions and catalysts required for high enantioselectivity appear to be extremely specific. Variation of the active phase, supports or modifier often leads to significantly reduced performance [2, 13, 14]. There is a general accord over the key role of cinchona modifier structure in the enantio-differentiation reaction, which depends on the

substituents at quinoline ring, quinuclidine moiety and the relative configuration of –OH group at chiral C9 position of a typical cinchona structure [15-18].

The complexity in product separation and non-reusability of the catalyst system make the process inefficient for industrial scale. These limitations can be eliminated by making a single unit catalyst system having chemically linked chiral modifier with the insoluble solid support in a confined environment, on to which Pt can be loaded afterwards to create a sufficient environment so that reactions should proceed enantioselectively.

Significant work has been done for the immobilization of the chiral ligands on to solid support to improve the reusability of the homogeneous catalyst [14, 19, 20]. Catalyst based on cinchona grafted silica has proven to be very successful i.e., dihydroxylation of olefin [21], Michael addition [22], synthesis of α -Amino Acids [23], enantioselective reduction with organometallic agents [24] and hydrogenation of ethyl pyruvate [25] and PPD [26-28]. The covalent anchoring of inducers suffers from the lengthy process involved in functionalization of inducer and effective covalent anchoring onto the support.

In this paper, the immobilisation of CD covalently anchored onto mesoporous titanate nanotubes (TNTs) supports, along with their applications in the enantioselective hydrogenation of PPD are reported. TNTs, kind of widely recognized mesoporous nanostructures with large and accessible channels as well as good thermal and hydrothermal stability, high specific surface area and ion-changeable ability. The TNTs can be prepared by different procedures such as assisted–template method [29], the sol–gel process [30], electrochemical anodic oxidation [31], and hydrothermal treatment [32].

As an extension of our previous studies [28], we attempt to show some insight on the role of the mesostructured support on activity and selectivity of PPD heterogeneous hydrogenation in semi-batch systems. The study is focused on the direct immobilization using a top–down approach with 11-trimethoxysilyl-cinchonidine (TMS-CD). The synthetic procedure towards the supports synthesis and modification is shown in Scheme 1. The active phase deposition was performed using H₂PtCl₆ as a precursor at high H₂ pressure and room temperature. Some important reaction parameters, such as the surface modifier concentration, PPD concentration, H₂ pressure and solvent, which have been less

studied in the literature, were investigated in detail to optimise the enantioselectivity and catalytic performance.

2. EXPERIMENTAL SECTION

2.1 Materials

All air-sensitive reactions were performed under an inert atmosphere (Ar) in a Schlenk flask. Tetrahydrofuran (THF) and toluene were dried in metallic sodium/benzophenone; triethylamine (TEA) was distilled at reduced pressure prior to use. Cinchonidine (96% Aldrich[®]), trimethylchlorosilane (TMCS), trimethoxysilane (TMS), platinum cyclooctadienyl (II) chloride (Pt(COD)Cl₂), anhydrous sodium sulphate (Na₂SO₄), titanium(IV) oxide, TiO₂-anatase (99% AlfaAesar), H₂PtCl₆.6H₂O (40%Pt), sodium hydroxide (NaOH), and the solvents (cyclohexane, ethanol, ethyl acetate) were used as received.

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Scheme 1. Synthetic route for CD modification and catalysts preparation.

2.2 TNTs synthesis and activation

The synthesis of the TNTs was carried out by hydrothermal process. For this purpose, 1.25 g of the anatase-TiO₂ was dispersed in 20 mL of NaOH 10 molL⁻¹. The mixture was placed into a hydrothermal reactor at 120°C for 24 h with constant agitation. After, the mixture was washed with an acidic solution HNO₃ 0.1 molL⁻¹ and later with distilled water. Finally, the obtained TNTs were dried at 80°C for 12 h. The activation was performed primarily to increase the surface concentration of Ti-OH groups because they are responsible for the immobilization of TMS-CD, as reported in our own previous works [26, 27]. Activation of the TNTs surface was performed in a round-bottom flask in which 3.0 g of support was

mixed with 24 mL of 1,4-dioxane and 3 mL of aqueous solution of 3.1 molL⁻¹ HCl. This system was stirred for 30 min at 80°C, filtered, and dried under vacuum (lower than 10^{-1} mbar) for 4 h at 120°C.

2.3 Preparation of 11-trimethoxysilyl-cinchonidine (TMS-CD)

The modification of CD and the subsequent later hydroxylation were performed as reported in our previous works [26, 27]. Briefly, an ice-cooled solution of CD in THF containing TEA was added dropwise to the TMCS. The reaction mixture was stirred for 20 h at room temperature and then for 2 h at 60°C. The product was extracted with chloroform and washed with water. The obtained product was hydroxylated with the Pt(COD)Cl₂ catalyst precursor and TMS (TMS/catalyst = 120, mole ratio) at 40°C K using toluene as the solvent. The reaction mixture was stirred for 5 h at 90°C under a N₂ atmosphere. Purification was performed by flash chromatography (hexane-acetone-TEA = 40:18:1).

2.4 Synthesis of modified TNTs

Five supports were prepared with different amounts of CD (1, 5, 10, 15, and 20 wt%), simulating the CD fractions that are added in traditional systems. A 2.0 g sample of activated TNTs and the appropriate amount of TMS-CD in toluene were added into a round-bottom flask, and the volume of the system was then brought to 50 mL with solvent (see Scheme 1). The reaction was refluxed for 12 h and later filtered and washed twice with 40 mL toluene and 20 mL chloroform. The solid was dried in a furnace for 1 h at 80°C. Subsequently, the solid was treated by refluxing in a mixture of methanol/THF for 20 h and was then washed with 100 mL of n-pentane. Finally, the solids were dried under vacuum for 4 h at 120°C. All the samples of the modified supports were denoted as TNT-CD[x], where [x] is the nominal TMS-CD wt% and, in the case of 0, corresponds to TNTs-activated support.

2.5 Catalysts preparation

The catalysts (1.0 g) were prepared to obtain 1 wt% Pt loading using the five modified supports and activated TiO₂. These were labelled as 1%Pt/TNT-CD[x], with [x] = 1-20. The methodology is similar to that reported in our previous work [27]. The support was dispersed in 50 mL of deionised water in a Teflon container, and the appropriate amount of H₂PtCl₆·6H₂O was added. After 1 h, 0.5 mol L⁻¹ NaOH was added (OH⁻:Pt = 6) and sealed in a stainless steel batch reactor. The pressure was adjusted to 40 bar H₂ for 2 h under constant magnetic stirring at 25°C, obtaining the reduced supported metal. Then, the solid was filtered off and washed to constant values of pH and conductivity. Finally, it was dried in a vacuum oven at 100°C for 1 h and stored in a desiccator under N₂ atmosphere prior to the catalytic test.

2.6 Catalyst characterisation

Elemental analyses of C, H, and N were performed on a LECO CHNS-932 analyser. NMR spectra for ¹H and ¹³C {¹H} were obtained on a Bruker AMX-300 spectrometer (300 MHz for ¹H, 75 MHz for ¹³C) using trimethylsilane as an internal standard. The results obtained from the NMR of ¹H and ¹³C were compared with those reported by Leino *et al.* [33, 34]. Solid-state ¹³C and ²⁹Si CP NMR spectra were recorded at 100.6 MHz and 79.49 MHz, respectively, using a Bruker AV 400 WB spectrometer. Diffuse reflectance infrared Fourier transform (DRIFTs) spectra were performed on a JASCO FT/IR-6300 fitted with an MCT-A detector and a KBr beamsplitter within the range of 4000-650 cm⁻¹. Approximately 0.020 g of the sample was loaded into a diffuse reflectance (DRIFTS) reaction cell provided by Harrick (Praying Mantis model). Before any measurements were performed, the sample was heated for 1 h at 150°C in He flowing at 30 mL min⁻¹ and then cooled to room temperature. For all the measurements, spectra were a composite of 64 scans with a resolution of 4 cm⁻¹. Prior to the run, backgrounds were collected by flowing He (at 30 mL min⁻¹) at the respective reaction temperature.

XRD patterns were recorded in a RigakuD/max-2500 diffractometer with Cu K α radiation at 40 kV and 100 mA. N₂ adsorption-desorption isotherms at -196°C were performed in a Micromeritics ASAP 2010 apparatus. Specific surface areas were determined by the BET

(Brunauer-Emmett-Teller) equation, using adsorption data in the relative pressure range of 0.05 to 0.3, and pore-size distributions were estimated using the BJH method. TG studies were conducted in a Mettler Toledo Thermogravimetric TGA/SDTA 851 using an O₂ flow of 25 mL min⁻¹ and a heating rate of 5°C min⁻¹ from 25 to 800°C. Dismissing the adsorbed water in TNTs, the mass loss diminishes allow the determination of the grafting density of functionalized TNTs by the following equation:

$$G = \frac{\frac{m_{TNT-CD[x]}}{100 - m_{TNT-CD[x]}} - \frac{m_{TNTs}}{100 - m_{TNTs}}}{M_{TMS-CD} \cdot S_{BET}}$$

where $m_{TNT-CD[x]}$ is the mass loss percentage of CD on TNTs and m_{TNTs} is the mass loss corresponding to the amount of physisorbed water in the TNTs (corresponding to the mass loss between 25 and 150°C; the amount of chemisorbed water (200 < T < 800°C) is not included in equation), M_{TMS-CD} is the molar mass of the TMS-CD and S_{BET} is the specific surface obtained by BET method [35].

The morphology and size of the crystallites were examined by transmission electron microscopy (TEM) images of the catalysts were obtained using a Philips electron CM200 microscope with an energy dispersive analyser and digital camera coupled to a high speed TVIPS FastScan F-114 model of 1024x1024 pixels and 12 bits. The samples for analysis were prepared by dispersion in ethanol/H₂O (1:1) and were deposited on a holey carbon/Cu grid (300 Mesh). Up to 300 individual metal particles were counted for each catalyst, and the surface area-weighted mean Pt diameter (d_p) was calculated from:

$$d_p = \frac{\sum_i n_i d_i^3}{\sum_i n_i d_i^2}$$

where n_i is the number of particles of diameter d_i . The size limit for the detection of Pt particles on samples was ca. 0.1 nm.

Photoelectron spectra (XPS) were recorded using a VG Escalab 200 R spectrometer equipped with a hemispherical analyser and using non-monochromatic Mg K_{α} X-ray radiation (hu = 1253.6 eV). The binding energies (BE) were calculated with respect to the C-component of the C1s peak fixed at 284.8 eV. Data analysis was performed with the "*XPS Peak*" software. The peaks were decomposed into a sum of Gaussian/Lorentzian (G/L = 90/10) after the subtraction of a Shirley type baseline. The surface Pt/Ti and N/Ti atomic ratios were estimated from the integrated intensities of the Pt 4f, Ti 2p, C 1s, and N 1s lines after background subtraction and were corrected by the atomic sensitivity factors [36].

2.7 Catalytic activity

The catalytic assays of PPD hydrogenation were performed in a stainless steel (100 mL) Parr-type semi-batch reactor at a concentration of 0.01 mol L⁻¹ of substrate using cyclohexane (25 mL) as solvent and stirring at 700 rpm under 40 bar of H₂ pressure. All catalytic runs were conducted in the absence of external mass transfer limitations. The catalysts were in the form of fine powders (> 30 μ m), assuming a negligible effect of pore diffusion limitations. In the catalyst mass studies, the (PPD/Pt) molar ratio was varied, the concentration of PPD was kept constant and the mass of the catalyst was modified. No important differences in the initial reaction rates were noted upon varying the catalyst mass. This indicated that gas-liquid and liquid–solid external mass transfer limitations were absent [8, 37]. The pseudo-kinetic constants (k) were calculated using a pseudo-first-order kinetic model for a batch reactor in similar conditions, as was reported by Toukoniitty *et al.* [9].

Reactants and products were analysed by gas chromatography and mass spectrometry using a GC-MS device (Shimadzu GCMS-QP5050) with a 30 m chiral β -Dex 225 column and helium as the carrier gas. The recycling assays were performed by filtering the catalyst from the reaction medium. The filtered catalyst was washed three times consecutively with chloroform to clean the surface and was then dried at 100°C for 24 h.

The turnover frequency (TOF) of the catalysts was calculated as follows:

$$TOF(min^{-1}) = \frac{Substrate \ hydrogenated \ (mol)}{Metallic \ Pt \ (mol) \cdot time(min)}$$

In relation to the selectivity of the catalysts, enantiomeric excess and regioselectivity have been defined as:

$$ee_{Cx}(\%) = \frac{[R]_x - [S]_x}{[R]_x + [S]_x} \cdot 100 \text{ and } rs = \frac{[R_{C1}] + [S_{C1}]}{[R_{C2}] + [S_{C2}]}$$

where [R] and [S] correspond to the concentration of the respective enantiomers, x is the number of the carbonyl group, and in the case of rs, of the alcohols of the different carbonyl groups.

3 RESULTS AND DISCUSSION

3.1 Support Synthesis and Characterisation

Fig. 1 displays the thermogravimetric mass changes for the different materials. For TNTs, a mass loss of 4.5 wt% in the 100 to 727°C range, which corresponds to the dehydroxylation and accounts for 2.5 mmol_{OH} g⁻¹. After the activation treatment, the TNT-CD[0] displayed a new slope in the range 100-727°C corresponding to 4 wt% mass, approximately 8.8 mmol_{OH} g⁻¹. The higher mass loss of pristine TNTs was detected in the range of 25–100 °C and it is mainly related to physically adsorbed water. However, silanized TMS-CD samples are less hydrophilic and, therefore, lower mass loss occurred in this temperature range. In the case of pristine TNTs the total mass loss was attributed completely to water loss and it was assumed that both interlayer (H₂O) and structural water (–OH) were only released at temperatures higher than 100°C [38].



Figure 1. TG curves for the synthesis of supports. Conditions: O_2 atmosphere to 25 mL min⁻¹ flow and temperatures in the range of 25-800°C.

The mass loss of functionalized TNTs was higher than that of pristine TNTs within the 100–200°C range, which might indicate an increase in the amount of interlayer water. On the other hand, the mass loss of functionalized samples was higher than neat TNT in the range of 200–800 °C indicating that TM-CD was primarily bonded to TNTs surface (not physically) and strongly suggesting that in this temperature range attached TMS-CD is lost. The supports modified with TMS-CD showed two steps of mass losses in the ranges 277–320°C and 380–550°C. The first mass loss corresponds to desorption of the water absorbed when the samples were exposed to the atmosphere prior to TG measurements. The first mass change is associated to the degradation of alkyl chains and the second corresponds to the quinoline aromatic ring oxidation [26].

Table 1 summarises the elemental analysis (EA) and TG data of the supports. The total content of TMS-CD anchored on the surface was lower than the nominal content, and the effect was more pronounced upon increasing the nominal content of the inducer. The calculations for EA were based on the N(at%) because it is the only vector of the real TMS-CD content anchored on TNTs, as reported in our previous works [26, 27].

EA and TG analysis showed a difference between the total grafted content of TMS-CD and can be explained in terms of the Ti-O-Si bonds on the TNTs surface. The 1,4-dioxane/HCl-

treatment increases the amount of hydroxyls on the surface, with different surface reactivity, such as protonated TNTs with $H_2Ti_3O_7$ stoichiometry with different acid/base character [39]. Thermic treatment of hybrid inorganic/organic materials under controlled atmosphere (N_2 and/or O_2) allows the synthesis of meta-stable phases such as oxycarbide glasses. In oxycarbide glass materials a part of the divalent oxygen in the TiO_2-SiO_2 composites, in our case TNTs-SiO₂, structure could be replace by tetravalent carbon. Silicon oxycarbide compounds of general formula $Ti_n-Si_{(m-n)}O_xC_y$ are amorphous and covalent solids containing Si–O, Ti-O, Ti-C and Si–C bonds [40]. In the TNT-CD[x] supports, the TMS-CD oxidizing thermic treatment provides a decrease in the mass loss, with respect to EA, attributed at formation of titanium-silicon oxycarbide species.

DRIFT spectra of the starter material (TiO_2 -anatase), TNTs and the modified supports, acquired in He atmosphere (30 ml/min) after heating the samples at 120°C are presented in Fig. 2. Although the intensity of the spectra of the two titanate samples are remarkably higher, both TiO₂-anatase and TNTs spectra exhibit a broad absorption region at 3600-2500 cm⁻¹, which correspond to adsorbed water molecules. These species show contributions of two different overlapping bands due to the vibrational modes of -OH groups involved in H-bonds from multilayer H₂O molecular arrangements. The band at lower wavenumbers (ca. 3220 cm⁻¹) can be assigned to -OH groups of tetrahedrally bonded water molecules, while the component at higher wavenumbers (ca. 3300 cm⁻¹) would correspond to hydroxyls from H₂O molecules with lower coordination [41]. The parent TiO2-anatase showed intense bands at 3674 and 3630 cm⁻¹ corresponding to vibrations of hydroxyl groups on the surface of TiO2. The presence of different components indicated the existence of more than one local structure for each type of hydroxyl species i.e., the stretching modes of free OH groups on Ti⁴⁺ of anatase, which interact with multilayer water [38, 41]. The other characteristic band at 1624 cm⁻¹ corresponds to bending mode of molecularly adsorbed water molecules.

In the case of TNTs, due to their considerably larger surface area, the intensity of the hydroxyl bands was more than double than in the case of TiO₂-anatase. Additional differences with respect to starter materials can be clearly observed when comparing the spectra of the two nanotubular samples and those of TiO₂-anatase. The band at 3690 cm⁻¹ can be related to hydroxyl in interaction with water, whereas TNTs surface. Finally, the peak at 3725 cm⁻¹ can be assigned to terminal hydroxyls. For TNT-CD[x] samples the ratio of intensities of the 3670 cm⁻¹ to the 3725 cm⁻¹ hydroxyls species increase after the activation treatment, as shown in figure 2(a). The intensity and width of this band can be explained by the different type of Ti-OH groups on the surface, in agreement with the TG results. With respect to the spectra profiles in figure 2(b), TNT-CD[x] with $[x] \neq 0$ displayed bands in the range 2956-2863 cm⁻¹ and 1540-1200 cm⁻¹. The first is associated with the C-H stretching vibrations of the quinuclidine heterocyclic ring, whereas in the second, the fingerprint bands of the TMS-CD are expected to occur. Upon increasing the nominal content of TMS-CD, the intensity of these bands increased, whereas the intensity of the band in the 4000-3000 cm⁻¹ range follows the opposite trend. Another band was detected at 1115 cm⁻¹, which can be assigned to the stretching vibration of the Ti-O-Si_{organic} bonds, and it would confirm the covalent immobilisation of TMS-CD on TNTs surface.



Figure 2. DRIFT of the supports modified with TMS–CD. (A) precursor TiO_2 -anatase, TNTs and TNTs-activated support; (B) TNT-CD[x] supports where the TNTs-activated support spectra was subtracted.

Modified TNTs supports were studied by solid-state ¹³C and ²⁹Si CP/MAS NMR spectroscopy and shown in Fig. 3(a) and 3(b), respectively. ¹³C NMR spectra displayed, for all the supports TNT-CD[x] with [x] > 1, resonances in the range of 20-70 ppm, which are characteristic of the quinuclidine moiety of TMS–CD [25-27]. Additional resonances at 118.2, 127.8 and 133.7 ppm were also observed, which correspond to the aromatic quinoline ring. In our previous works, an unusual ¹³C signal was observed at ca. -2.0 ppm, due to the Si-CH₃ moiety, but it was not detected in the TNT-CD[x] support. This could be explained by the acid/base nature of the Ti-OH groups of the prepared support.

Fig. 3(b) shows the ²⁹Si NMR for the TNT-CD[20]. This technique is very sensitive to Siatoms near -OH and/or -OR groups, and it is the standard characterisation method for silicate materials. Two signal types can be distinguished with this technique. The first type of signal arises from the anchored TMS-CD species that form bonds with the support/silicon alkoxides (-45 to 60 ppm denominated T^x signal, where x = 1, 2, or 3). The second signal type corresponds to siloxane/silane (-90 to -115 ppm denominated Q^Y signals, where y = 2, 3 or 4) that remain after hydrolysis/condensation the anchoring process. Because this support possesses the major TMS-CD content on the surface, the characteristic anchoring signals of the T² and T³ type at -48 and -85 ppm were detected, in agreement with the results we reported previously [26, 27]. For the Q signals, two silanols were detected, with a similar intensity between the T and Q signals. The two Q³ signals, which were attributed to free silanols, occurred at -101.1 and -107.3 ppm in different chemical environments.



Figure 3. Solid state CP-MAS NMR of the supports modified with TMS-CD. (a) ¹³C for TNT-CD[x] and (b) ²⁹Si for TNT-CD[20].

TNTs is an amphoteric metal oxide with acid-base pairs of Ti^{4+} (Lewis acid) and O^{2-} (Lewis base) ions on its surface [41]. These acid/base pairs can interact with the remaining free silanol groups and cause the signals that exhibit different chemical shifts. Consequently, we assumed that the resonance at -108.3 ppm corresponds to free silanol groups, whereas the resonance at -101.5 ppm can be assigned to the strong interaction with the inorganic phase. The characteristic resonance of a Si atom coordinated with one O atom from the TNTs surface (13 ppm) was not observed (Si impurities). This result is in agreement with the ¹³C NMR characterization and it would confirm the absence of impurities. The above characterization results confirm the proposed diagram suggested in Scheme 1.

3.2 Catalyst synthesis and characterization

Table 2 summarises the elemental analysis of the catalysts and the most relevant physicochemical properties. It can be observed that the TMS-CD content decreased with respect to the metal free counterparts in Table 1. This is due to a slight leaching of the inducer under the preparation conditions, as discussed in previous work [26, 27]. The nitrogen adsorption–desorption isotherm of starter material and TNTs produced from a N₂ are shown in Fig. 4. TNTs sample show type IV isotherms, associated to mesoporous materials, whose hysteresis loops can be described as intermediate of type H1 and H3. The isotherm has an obvious hysteresis loop at $P/P^0 = 0.45-1.0$, which indicates the

presence of mesopores in the materials. A hysteresis loop of type H1 is generally associated to mesoporous materials with uniform pores, while H3, characterized by the absence of a plateau at high relative pressures, is related to the presence of aggregates of laminar particles giving rise to slit-shaped pores [42].

For the structural parameters listed in Table 2, catalysts 1%Pt/TNT-CD[x] had a decrease in mesopore size and surface area. This behaviour indicated that the coverage of the pore surface with the TMS-CD functionalities led to an increase of the wall thickness [38, 42].

^(a)CD Maintained: (TMS-CD_{Catalyst}/TMS-CD_{Support}) x100% calculated from EA; ^(b)Determinated by N_2 Isotherm; (c)average sizes.

Based on the above characterizations, it could safely be concluded that the heterogeneous catalysts with ordered mesoporous structure could be obtained readily, by the synthetic strategy was employed in these cases. The surface area of pure TiO_2 -anatase was 142 m²g⁻¹, which is lower than the TNTs samples. In addition, the BET specific surface area 218 m²g⁻¹, which suggesting the sufficient surface for immobilisation sites.



Figure 4. N₂ adsorption–desorption isotherms of 77 K for 1%Pt/TNT-CD[x] catalysts. XRD pattern of the synthesized TNTs and TNT-CD[x] are shown in Fig. 5. It matches well with standard diffractogram of $H_2Ti_2O_5 \cdot H_2O$ (JCPDS: 47-0124), which coincides with the general molecular formula of protonated titanate ($H_2Ti_nO_{2n+1} \cdot xH_2O$) [43]. The TNTs pattern shows a notably lower intensity and the identified peaks at 10.7°, 24.9°, 44.0°, 48.9° and 62.2° can be assigned to the protonated layered titanate.



Figure 5. XRD patterns of the catalysts synthesized on modified supports. \blacklozenge corresponds to the H₂Ti₂O₅·H₂O (JCPDS: 89-4921) and metallic Pt (JCPDS: 04-0802).

The reflection at ca. 10.7° is attributed to the interlayer spacing in the nanotube wall. In the activated supports (TNT-CD[0]), no significant differences were observed with respect to the pristine TNTs, but a slight shift to larger angles of the very broad peak around 10°, which reveals a decrease in the spacing between the nanotube walls (d₂₀₀). The XRD patterns of the 1%Pt/TNT-CD[x] powdered samples were not observed a phase change for TNTs during Pt nanoparticles synthesis and deposition at high H₂ pressure. Only for the catalysts 1%Pt/TNT-CD[x] with $0 \le x \le 5$ displayed the Pt (1 1 1) crystal face diffraction was detected at 39.8° attributed to the contribution of Pt nanoparticles with sizes upper to 5.0 nm.

HR-TEM was used to estimate the TNTs shapes and the average Pt particle size, and some images are shown in Fig. 6. The TEM analyses evidenced that, while TiO₂-anatase is constituted by prismatic particles with size ranging from 50 to 15 nm. The hydrothermally synthesis reveals nanotubular morphology for TNTs. In fact, thermal calcination treatment, after synthesis and before to the TNTs activation, seems to promote the flawless scrolling of titanate sheets, as more uniform and well-formed nanotubes as was reported by Kasuga et al and Roy et al, respectively [30, 31]. For 1%Pt/TNT-CD[x] catalysts, the dark spots on the large TNTs surface were identified as Pt particles. The average Pt particle size in Table 2 is smaller than 2.0 nm for all the catalysts. The size of Pt particles on TNT-CD[x] displayed a similar distribution size, but dependent of the TMS-CD content, which is in agreement with results recorded in our results using γ -Al₂O₃ and SiO₂ materials [26, 27]. The stoichiometric addition of NaOH during the Pt nanoparticles synthesis allowed for a basic medium during the reduction process. In this case, TNTs was activated using an aprotic solvent medium to improve hydroxyl protonation and to avoid Ti-OH alkoxylation with protic solvent [44, 45]. These hydroxyl/hydronium groups enhance the metal retention on the support surface by ion exchange and complexing with the PtCl₆²⁻ metal precursor. In this case, the supports were contacted with a precursor solution at pH = 2.0. This phenomenon may be rationalised in terms of the surface properties of TNTS and the hydrolytic behaviour of PtCl₆²⁻in aqueous solution.







Figure 6. HR-TEM micrograph of the support and catalysts (A) TiO₂-anatase; (B) TNTs; (C) 1%Pt/TNT-CD[0]; (D) 1%Pt/TNT-CD[1]; (E) 1%Pt/TNT-CD[5]; (F) 1%Pt/TNT-CD[10]; (G) 1%Pt/TNT-CD[15] and (H) 1%Pt/TNT-CD[20].

In the case of TNTs, the zero point charge (pH zpc) is 2.4 [38]. Hence, at more acidic pH values, the surface is positively charged. In an aqueous solution, $PtCl_6^{2-}$ undergoes a sequential hydrolysis to give various hydrolytic products, as mentioned in our previous reports:

$$PtCl_6^{2-} + xOH^{-} \rightarrow [Pt(OH)_xCl_{6-x}]^{2-} + xCl^{-}$$

Under an acid medium, the positively charged surface of TNTs would explain the anchoring behaviour of the platinum complex [28]. In the first step occurs ion exchange process between support surface and $PtCl_6^{2-}$ precursor ions. During the increase of pH allows the reaction of the $PtCl_6^{2-}$ precursor to give mixed $[PtCl_{6-x}(OH)_x]^{2-}$ species. A series of ligand substitution reactions of $[PtCl_6]^{2-}$ in aqueous hydroxide medium and, at the same time, the TNTs surface change, result in anionic species, such as Ti-O⁻. This charged oxygen is basic and allows the substitution of the OH- groups from the $[PtCl_{6-x}(OH)_x]^{2-}$ complex for Ti-O⁻, as shown in scheme 2. However, during the precursor reduction, the H₂ is consumed and consequently leads to a decrease of the pH. This is the reason for using Pt:OH = 6 or a stoichiometric quantity of hydroxyl groups to give a pH neutral solution.



TMS-CD modified sites

Scheme 2. Schematic deposition of metal [PtCl₆]²⁻ complexes onto TNTs surfaces.

On a positively charged surface of TNTs, the concentration of $[Pt(OH)_xCl_{6-x}]^{2^{-}}$ hydrolysed products is expected to be adsorbed on the surface by the Ti-O-complex bond, which in turn leads to a fast deposition rate that results in a smaller size of platinum particles. The catalyst prepared on the activated support (TNT-CD[0]) displayed small particle sizes, reaching approximately 2.0 nm, and a narrow distribution of particle size values. The organic molecule does influence the Pt cluster formed during the metal reduction. CD at acidic pH (pKa = 5.8) is positively charged by quinuclidine ammonium charge (R₃-NH⁺) [46]. In the supports, the increase of TMS-CD content provides more cationic sites for ion exchange with the anionic precursor. Given these conditions of catalyst preparation, a preferential deposition towards immobilized TMS-CD sites provides a decrease in the nanoparticles sizes distributions.

The oxidation states of the species on the catalysts surface were investigated by XPS. Table 3 compiles the Pt $4f_{7/2}$, N 1s, O 1s and Ti $2p_{3/2}$ binding energies (BE) for all the

catalysts under study with the corresponding contribution to the overall signal in parentheses. The Pt 4f spectra of the Pt/TNT-CD[x] catalysts showed only one doublet, with the most intense Pt4f_{7/2} component placed at 72.0 eV as shown in Fig 6. After precursor reduction in H_2 at room temperature and 40 bar, the metallic clusters displayed small particle sizes.

The electronic properties of these very small Pt clusters on TNTs regularly displayed only the presence of Pt⁰ species [47]. The Pt $4f_{7/2}$ BE appears at 72.0 eV. This value is close to that reported by Sato *et al.* for similar TNTs supported Pt particles and corresponds to a positive shift of 1.0 - 0.5 eV compared to the most common value measured for bulk metallic platinum Pt⁰ (71.0-71.5 eV) [47]. Such positive shifts can be explained by strong support-metal interactions. Charge transfer from the particle to the support, especially in systems with metallic particles on reducible metal oxides, can alter the electronic properties of the metallic active phase. Small particles also have a large number of surface atoms with reduced coordination number. This feature is known to induce positives or negative binding energy shifts relative to the value measured for the bulk metal [48]. The main $\Delta BE_{Pt(4f7/2)}$ detected for the catalyst supports on 1%Pt/TNT-CD[x] showed a similar trend suggesting that the Pt clusters are in zero state but with an electron-deficient nature.



Figure 7. XPS spectra for the catalysts supported on TNT-CD[x]. The N1s is another important signal in determining the nature of TMS-CD on the surface. For aromatic sp² or aliphatic sp³–hybridised nitrogen (N_{neutral}), characteristic peaks at 399.0–399.8 eV were found [49]. In our case, two contributions for N 1s peak were detected at 399.8 – 399.9 and 401.3–401.6 eV. The first corresponds to N_{neutral} typical for non–adsorbed TMS-CD molecules [50, 51]. The second can be attributed to positively charged nitrogen (N_{ionic}), in agreement with previous results reported by Bonello *et al.* and Evans *et al.* [52, 53]. The N_{neutral} and N_{ionic} signals correspond to both nitrogen atoms from TMS-CD, and these were not resolved so that only an average value was determined. In addition, the chemical shift for the second N_{ionic} signals can be attributed to the H₂Ti_nO_{2n+1}·xH₂O surface interaction with quinuclidinic and quinolinic N atoms due to an acid/base effect induced by H bond formation (see table 3). In our recent report, using TiO₂-anatase as support in Pt/TiO₂ modified catalysts, a decrease of ΔBE_N was detected with the increase of TMS-CD on the support surface [28]. In 1%Pt/TNT-CD[x] catalysts, convolution of the Pt⁰/Pt⁶⁺ contribution in Pt 4f_{7/2} signals was not detected because the

strong metal support interaction provides electron-defficient state Pt^{δ^+} for metallic nanoparticles. The active phase did not show a TMS–CD–platinum retrodonation because the ΔBE_N is constant in all the catalysts, nevertheless $N_{neutral}$ and N_{ionic} species contribution change with the increase of the TMS-CD on the TNTs surface. This behaviour can be explained by inducer-TNTs acid/basic interaction and the confinement effect in the nanotubular structure. The TMS-CD immobilisation process can graft inside the tubes and/or outside the tubes. Both dispositions provide different environmental interaction of hydroxyl groups with the N basic atoms from the TMS-CD. Fig. 8 shows difference between N_{ionic} and $N_{neutral}$ contributions (ΔN_{XPS}) in relation with the nominal content of TMS-CD in all the synthetized catalysts. For the systems 1%Pt/TNT-CD[x] with $0 < x \le 5$ an increase in modifier surface concentration showed an increase in this ΔN_{XPS} attributed to the contribution of Ti-OH species inside of the tubes. The disposition and surface concentration of hydroxyl groups on the internal nanotubes walls provides a stronger acid/base interaction with the N atoms from TMS-CD, until wall thickness saturation (Ti–O–Si bond formation).



Figure 8. ΔN_{XPS} for the N 1s determinate by XPS for TMS-CD anchored on different TNTs supports in relation with real TMS-CD content.

After internal nanotubes saturation, the modifier was anchored, preferably, outside of the nanotubes and the acid/base interactions are most weak. This behaviour is in agreement with the S_{BET} and pore volume values displayed in table 2.

The N/Ti surface ratio shows an increase with the increase of TMS-CD on the surface due to the coverage of the support by inducer in agreement with EA and TG results. The high increase of Pt/Ti ratio can be attributed at: (1) the formation of Pt nanoparticles from the precursor compound finely dispersed (see Fig. 6) and (2) a preferential outside nanotubes deposition of Pt, compared to the unmodified support, as the TMS-CD content increase on the TNTs surface.

3.3 Enantioselective hydrogenation of PPD

3.3.1 TMS-CD Effect

The reaction scheme for the hydrogenation of PPD is displayed in Scheme 3. As the figure shows, the complete reaction scheme is comprised of seven components. The influence of the TMS-CD amount on the catalytic performance in the asymmetric hydrogenation of PPD with Pt/TNT-CD[x] catalysts was investigated. Fig. 9 shows the profiles of conversion vs. time in PPD hydrogenation. A pseudo–first–order kinetics with respect to PPD was found in all cases, reaching conversion levels over 98% at 240 min of reaction for the 1%Pt/TNT-CD[10]. All of the catalysts were enantioselective for (R)-1-hydroxy-1-phenylpropan-2-one (1R-PP) and (R)-2-hydroxy-1-phenylpropan-1-one (2R-PP), no other hydrogenated products were detected.



Scheme 3. Hydrogenation route of PPD.

With respect to enantioselectivity, the reaction with activated and bare TNTs displayed the racemic mixtures, although the conversion reached 60%. On the catalysts supported on TNT-CD[x] with [x] > 0, an increase in the conversion to PPD was detected suggesting that the hydrogenation was a "ligand-accelerated" reaction similar to previous studies reported by Margitfalvi *et al.* [54-56]. According to these authors, this feature can be explained by the formation of a weak modifier–substrate complex for the supported metallic catalysts where the inducer was added *in situ*.



Figure 9. Activity curves based on PPD conversion for 1%Pt/TNT-CD[x] catalysts. Reaction conditions: PPD concentration: 0.01 mol L⁻¹, catalyst mass: 0.050 g, P_{H2}: 40 bar, stirring speed: 700 rpm, solvent: cyclohexane.

Table 4 shows the conversion levels and the pseudo-constant rate, k_g . An increase of the TMS–CD content resulted in higher surface coverage, and an enhancement of the catalytic performance until 1%Pt/TNT-CD[x] with x = 10, at superior nominal content a decrease on the catalytic activity was detected. This trend can be explained for internal nanotubes saturation by the modifier anchored as was demonstrated in the previous section. This behaviour is similar to that previously reported by Reyes *et al* [6, 57] in the same reaction where the CD was added *in situ* using metallic catalyst supported in MCM-41 mesostructures.

^(a)240 minutes of reaction

^(b)average values.

 ${}^{(c)}k_g = k_{1R} + k_{1S} + k_{2R} + k_{2S}$

 $^{(d)}k_g$ was calculated until the diols products detect at 80% of conversion and S_{diols} = 53.5% at 240 minutes.

Fig. 10 shows the evolution of the enantiomeric excess (ee) vs. conversion. All the catalysts were selective for the hydrogenation of the carbonyl groups (see Scheme 3). 1R-PP was the main reaction product, and the ee_{C1} was similar to those reported for systems in which the chiral inducer was added *in situ* and adsorbed on the surface of the catalyst [58, 59]. All the system showed different trend in the ee during the reaction. In the catalysts 1%Pt/TNT-CD[x] with x = 0 and 1 only the carbonyl adjacent to the phenyl group (C1) was hydrogenated given the correspond products. When increasing the TMS-CD amount on the TNTs surface, the ee was further improved to a maximum of 38% for the catalyst 1%Pt/TNT-CD[15].



Figure 10. Enantiomeric excess vs. PPD conversion for 1%Pt/TNT-CD[x] catalysts. Reaction conditions: PPD concentration: 0.01 mol L⁻¹, catalyst mass: 0.050 g, P_{H2}: 40 bar, stirring speed: 700 rpm, solvent: cyclohexane.

The confinement effect inside of the nanotubes enhance of hydrogenation rate of PPD. In 1%Pt/TNT-CD[x] with x = 5 and 10 the concentration of TMS-CD on surface saturate the active sites promoting the non-parallel adsorption of PPD (for η bond formation between Pt nanoparticles and the π aromatic cloud of the phenyl group), decreasing the effective formation of modifier–substrate complexes over

metallic modified sites and enantioselection capacity. This trend is in agreement with rs values showed a low hydrogenation rate of the carbonyl adjacent to the phenyl group (C1), with values of 18 for both systems in line with studies reported by Toukoniitty *et al.* [8, 9, 34]. Finally, the catalyst 1%Pt/TNT-CD[10] showed 44% of enantiomeric excess at the maximum conversion (98%). This value cannot use as real value of enantioselection for this reaction because the hydrogenation of the hydroxyl-ketones was detected. The appearance of RR-diols, SS-diols, and meso diols, as well as an enhancement in ee by the rate of hydrogenation of 1S-FP is higher than 1R-FP, as reported by Toukoniitty *et al* [9, 11]. At higher TMS-CD contents, the conversion and ee value decreased. The 1%Pt/TNT-CD[x] with x = 15 and 20 showed only hydrogenation the adjacent to the phenyl group (C1), with 1R-PP being the preferred product. Both supports show the highest loading of TMS-CD (see table 2) and shows a

decrease in catalytic activity by blocking the entry of nanotubes to active sites located inside the pores by repulsive steric interaction. In these cases, the activity of the catalyst was provided only for the metallic sites located outside of the nanotubes.

3.3.2 Effect of H₂ pressure

After finding the most enantioselective catalytic system, i.e., Pt/TNT-CD[15], the effect of hydrogen pressure was negligible where the hydrogen pressure was varied from 10 to 40 bar. Fig 11 shows the TOF and selectivity as a function of H₂ pressure. The surface H₂ concentration may directly influence the reactant adsorption and, thus, enantioselectivity. An increase in H₂ pressure (from 10 to 40 bar) markedly effects the TOF but only slightly effects the ee. The TOF increases with increasing pressure. The reaction proceeded slowly at 10 bar; the PPD conversion was only 66% after 240 min. However, at 60 bar, the PPD conversion was 99% over the same time period, which indicates that hydrogen adsorption is mainly non-competitive.



Figure 11. Selectivity and TOF for PPD hydrogenation on 1.0%Pt/TNT-CD[15] catalyst at different H₂ pressures. Reaction conditions: PPD concentration: 0.01 mol L⁻¹, catalyst mass: 0.050 g, stirring speed: 700 rpm, solvent: cyclohexane. Means value of enantiomeric excess (ee), conversion levels, diols selectivity and rs was quantified at 240 minutes of reaction.

The approximately linear plot of TOF values versus hydrogen pressure indicates first-order kinetics with respect to hydrogen pressure. At pressures > 40 bar, other hydrogenation products were detected. At the TMS-CD concentration used, the PPD phenyl ring was not hydrogenated to a cyclohexyl ring; thus, undesirable products were formed both from the reactant and each product, which yielded seven hydroxyl products. It can be concluded that C=O non-selective hydrogenation is generally more favourable at higher pressures due to the short residence time of PPD in the metallic sites outside of channels.

3.3.3 Effect of the solvent

The effect of solvents with dielectric constants ranging from 2 to 25 (values of pure solvents) have been included in this study for the hydrogenation of PPD catalysed by 1%Pt/TNT-CD[10]. The results are displayed in Fig. 10 and correspond to a qualitative model including the enantioselectivity and the dielectric constant of the pure solvents, similar to that proposed in our previous reports [26-28, 57]. The highest activity was observed in ethanol, and very low reaction rates were obtained in tetrahydrofuran, whereas relatively high conversion levels were obtained in the other solvents in this

study. In terms of enantioselectivity, among the solvents investigated, toluene led to the best e.e. values of 38% at 85% of conversion.



Figure 12. Curves of the enantiomeric excess and PPD conversion vs. dielectric constant for PPD hydrogenation on 1%Pt/TNT-CD[15] at different solvents. Reaction conditions: PPD concentration 0.01 mol L⁻¹, P_{H2}: 40 bar, catalyst mass: 0.050 g and stirring speed: 700 rpm.

Conversely to previous reported results for Pt supported TMS–CD–TiO₂ catalysts, toluene showed a higher conversion levels in comparison to cyclohexane [28]. Both solvents have similar dielectric constants and have shown high conversion and ee in PPD hydrogenation using the same reaction conditions. In our case, the electronic nature of Pt⁺⁶ nanoparticles provided an enhancement in PPD adsorption in toluene as solvent by dipole-induced interactions with the active phase surface (π aromatic bonds), increasing the conversion levels and ee. The ee was almost 33% in cyclohexane and decreased to 15% in ethanol. Finally, ee decreased non-linearly with increasing solvent dielectric constant, which was attributed to the interactions between solvents and the population of optimum TMS-CD conformers on the surface. On the other hand, these results do not show a clear correlation between the catalytic performance and solvent polarity, in agreement with similar studies reported by Toukoniitty *et al.* for commercial Pt, Pd and Rh/γ-Al₂O₃ supported catalysts [3].

3.3.4 Recycling

Fig. 13 shows the variation of the conversion and ee levels as a function of the number of reaction cycles for the catalyst 1%Pt/TNT-CD[15]. Between cycles, the catalyst was washed with chloroform to remove the organic matter that could have been adsorbed on the support and the TMS-CD from leaching [4]. All the cycles show a pseudo-first-order kinetics during the hydrogenation reaction. As the number of reaction runs increased, the activity decreased, reaching values of 37% in the last cycle.





Table 7 shows the catalyst characterization after the last cycle. N(at%) shows constants values, suggesting that non-leaching of the inducer was detected. The active phase showed constant values for the Pt BE, but a high decrease of Pt/Ti surface atomic ratios after the last cycle, attributed at a Pt nanoparticles leaching. The nanoparticle distribution sizes displayed a similar trend and regular shapes as fresh 1%Pt/TNT-CD[15] catalyst. In this way, non-sintering but leaching of nanoparticles was assumed in all the runs. For 1%Pt/TNT-CD[15] catalyst, we assumed only the contribution of Pt nanoparticles located outside of the nanotubes. For this reason the leaching was more important in the recycle studies.

4. CONCLUSIONS

Nanotubular TiO₂ based catalyst were synthesised for the enantioselective hydrogenation of PPD. Cinchonidine was tethered directly with prior silanisation modification over activated TNTs. The characterisation data provide evidence of the covalent immobilisation of cinchonidine. The HR-TEM images and XPS demonstrated that the cinchonidine content affect the active phase dispersion and particle size distribution. It can be deduced from the XPS results that the Pt nanoparticles exhibited a positively charged surface, which was attributed to the metal deposition method and the strong interaction with the TNTs surface. The 1%Pt/TNT-CD[x] catalysts displayed relatively high conversion and regular ee values (38%). The catalyst with [x] = 15 presented performances similar to those previously reported for a commercial Pt/Al₂O₃ catalyst, where untethered cinchonidine was used. The effect of the H₂ pressure and solvents indicated that the reaction conditions were important in controlling the activity and enantioselectivity. The solvent effect studies showed non-linear correlation between enantiomeric excess and the dielectric constant of the pure solvent. The most selective catalyst showed poor reusability under optimum conditions and deactivation by hydrogenation of TMS-CD and Pt leaching after the fifth cycle.

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Table 1. Elemental analysis and TMS-CD content determinate by TG of the synthesized supports.

	TMS-CD											
Comulo	Added				-	Yield						
Sample	amount (μmol m ⁻²) ^a	C(at%)	H(at%)	N(at%)	Inducer content (wt%)	Grafted amount (mmol m ⁻²) ^(a)	Inducer content (wt%)	Grafted amount (mmol m ⁻ ²) ^(b)	(%) ^{c)}			
TNT- CD[1]	14.1	1.28	1.15	0.07	1.0	0.01	0.5	0.01	100			
TNT- CD[5]	75.3	2.94	1.25	0.31	4.4	0.07	2.0	0.03	87			
TNT- CD[10]	157.2	4.14	1.31	0.41	5.9	0.09	3.4	0.05	59			
TNT- CD[15]	262.4	4.58	1.44	0.48	6.9	0.12	4.0	0.07	46			
TNT- CD[20]	365.3	5.16	1.31	0.54	7.8	0.14	5.9	0.11	39			

Table 2. Elemental analysis and physicochemical properties: S_{BET} , pore diameter and metallicnanoparticles diameter of 1%Pt/TNT-CD[x] catalysts.

Sample	N (at%)	TMS-CD (wt%)	CD Maintained ^(a) (%)	S _{BET} (m²g⁻¹)	Pore Diameter ^(b) (nm)	Pt size ^(c) (nm)
TiO ₂	-	-	-	142	9.8	-

TNTs	-	-	-	218	7.2	-
1%Pt/TNT-CD[0]	-	-	-	207	7.2	1.4 ± 0.8
1%Pt/TNT-CD[1]	0.07	0.9	92.9	176	7.0	1.4 ± 0.2
1%Pt/TNT-CD[5]	0.20	2.8	55.7	165	7.1	1.6 ± 0.6
1%Pt/TNT-CD[10]	0.29	4.1	40.7	158	6.9	1.6 ± 0.8
1%Pt/TNT-CD[15]	0.32	4.6	30.5	142	6.7	1.7 ± 0.7
1%Pt/TNT-CD[20]	0.44	6.3	31.1	136	6.7	1.7 ± 0.4

 Table 3. Binding energies (eV) of internal electrons and atomic surface ratio of 1wt%Pt/TNT-CD[x]

 catalysts.

Catalyst	Pt 4f _{7/2}	N 1s	Ti 2p _{3/2}	0.4	D. /T	s. / ** *	
	(eV)	(eV)	(eV)	O 1s	Pt/ II at	N/ II at	
1%Pt/TNT-CD[0]	72.0		458.6	529.8 (83)	0.0087	-	-
				531.8 (17)			
1%Pt/TNT-CD[1]	72.1	398.6 (43)	458.6	529.9 (80)	0.0224	0.0665	0.0665
	, 2.1	400.9 (57)	450.0	531.7 (20)		0.0005	
		398.7 (37)	450.0	530.0 (82)	0.0226	0.4024	
1%Pt/INT-CD[5]	/2.1	401.0 (63)	458.6	531.7 (18)	0.0236	0.1031	
		398.6 (38)		529,9 (83)			
1%Pt/TNT-CD[10]	72.0	400 9 (62)	458.6	523.5 (03)	0.0248	0.1118	
		400.5 (02)		531.8 (17)			
1%Pt/TNT-CD[15]	72.1	398.7 (41)	458.6	529.9 (85)	0.0273	0.1347	

		401.0 (59)		531.7 (15)		
1%Pt/TNT-CD[20]	72.0	398.7 (43) 401.0 (57)	458.6	530.0 (81) 531.8 (19)	0.0344	0.1405

Table 4. Catalytic data for PPD hydrogenation over 1%Pt/TNT-CD[x] catalysts. Reaction conditions: PPD concentration: 0.01 mol L⁻¹, P_{H2}: 40 bar, catalyst mass: 0.050 g, stirring rate: 700 rpm, solvent: cyclohexane at 25°C

TMS-CD	Conversion ^(a)	TOF	ee _{C1} ^(b)	ee _{c2} ^(b)	rs ^(b)	k _g (c)	k _{1R}	k _{1S}	k _{2R}	k _{2S}
nominal	(+ 1 5%)	(min ⁻	(±	(±		(min ⁻	(min ⁻	(min ⁻	(min ⁻	(min ⁻
(wt%)	(± 1.5%)	¹)	0.5%)	0.5%)		¹ g⁻¹)	¹ g⁻¹)	¹ g⁻¹)	¹ g⁻¹)	¹ g⁻¹)
0	71.1	33	0.9	-	-	0.092	0.046	0.046	-	-
1	77.5	70	22.4	-	-	0.130	0.082	0.048	-	-
5	83.2	104	27.9	18.3	18.7	0.156	0.080	0.042	0.021	0.013
10 ^(d)	98.4	165	37.8	21.8	18.2	0.346	0.222	0.099	0.015	0.010
15	91.5	135	33.8	-	-	0.250	0.170	0.080	-	-
20	86.1	128	28.7		-	0.192	0.125	0.067	-	-

Table 5. EA, HR-TEM mean Pt sizes and XPS data for recycles of the catalyst 1%Pt/TNT-CD[15]. Reaction conditions: PPD concentration: 0.01 mol L^{-1} , catalyst mass: 0.070 g per cycle, P_{H2} : 40 bar, stirring rate: 700 rpm at 25°C.

		TMS-CD	Pt 4f _{7/2} N1s				Pt size ^(b)	
Cycle	N(%) ^(a)	(wt %)	(eV)	(eV)	Pt/Ti at	N/Ti at	(nm)	
First	0.32	4.6	72.1	398.7 (41) 401.0 (59)	0.0273	0.1347	1.7 ± 0.7	

				398.6 (37)			
Final	0.31	4.5	72.0		0.0184	0.1012	1.5 ± 0.4
				401.1 (63)			

^(a)average value from two measurements. ^(b)Average diameter size

The XPS shows the presence of two types of surface nitrogen, N_{neutral} and N_{ionic},. The remaining anchored chiral inducer was slightly hydrogenated in the quinoline cycle of the TMS–CD because a slight ΔBE_N shift to a higher value was detected. TMS–CD hydrogenation on the support contributed to the decrease of activity because they might be interfering with the adsorption of the substrate on the remaining active sites. Subsequently, this blockage poisons the active sites close to the hydrogenated-immobilised modifier and these sites leads to a racemic mixture and thus decreasing ee values.