

Examination of the surface chemistry of activated carbon on enantioselective hydrogenation of methyl pyruvate over Pt/C catalysts

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Abstract

Pt/C catalysts were prepared on oxidized activated carbons. Different oxidation treatments were used both in liquid and gas phase using HNO_3 and 5% O_2/N_2 as the respective oxidizing agents. Thus, different surface chemical properties were achieved. The enantioselective hydrogenation of methyl pyruvate with (–)-cinchonidine as modifier revealed that the catalytic activity is dependent on the concentration of the surface oxygen remaining after activation as measured by XPS. It is suggested that it is a result of the increase in the carbon hydrophilicity that would enable the reactants to go through the catalyst. It is also suggested that the active sites created by the decomposition of the functional groups would allow hydrogen chemisorption and, therefore, the C=O polarization via hydrogen bond interaction. The chemical nature of the surface functional groups did not seem to influence either the catalytic activity or enantioselectivity. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

A wide range of products, such as pharmaceuticals and agrochemicals, can be listed as examples of compounds whose biological activity is strongly attached to their configuration, i.e., to a specific enantiomer. The most significant studies focused on the development of suitable catalysts for chiral compounds production were published over the last few years [1–8]. Biocatalysts have drawn much attention as they lead to high enantioselectivities. The use of heterogeneous catalysts, on the other hand, is still limited. Con-

ventional catalysts in the presence of a chiral compound can drive, in some cases, the reaction for the formation of a preferential enantiomer. Unfortunately, however, the use of modified heterogeneous catalysts is effective only over a few systems, Ni/tartrate/ β -ketoesters and Pt/cinchona/ α -ketoesters hydrogenation.

Regarding the α -ketoesters hydrogenation, most of the reports have been focusing on the mechanistic aspects of substrate–modifier interaction [1–3,5,9–11] even though some studies related to the preparation of Pt/ Al_2O_3 and the effects of their textural and bulk structural properties on activity and enantioselectivity have also been reported [6,7]. Nevertheless, there is a lack of discussion on the nature of the other supports, especially those that have been increasingly used in the preparation of catalysts for the fine chemicals production such as carbons.

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Carbon-supported catalysts have drawn attention as it is possible to tailor the physical and surface chemical properties of the carbons. Indeed, the surface chemistry of such supports is widely studied and published in the literature [12–14] and it is well known that the nature of the functional groups on the carbon surface can strongly affect the physical and chemical characteristics of a catalyst. Despite such knowledge, the features of carbon-supported catalysts and their influence on enantioselective reactions are hardly described in the literature. Recently, some carbon support effect was investigated in the enantioselective hydrogenation of a C=C double bond over Pd catalysts [8].

In this work, the studies were focused on liquid phase hydrogenation of methyl pyruvate on different activated carbon supported platinum catalysts. Enantioselectivity was induced using (–)-cinchonidine as a modifier. This pair substrate/modifier is by far the most studied system in the literature and enantioselectivity as high as 95% has been reported over Pt/Al₂O₃ [4]. Hence, this particular reaction has been pointed out as the most suitable one to investigate the factors that affect the enantiodifferentiation process [15]. The aim of this work is to describe and discuss the influence of the chemical surface properties of activated carbons used as support on the catalyst performance.

2. Experimental

2.1. Supports

The following supports were used for the preparation of platinum catalysts:

1. a commercial activated carbon (ROW 0.8 s NORIT) after being extensively washed with hydrochloric acid 2 M and subsequently with distilled water until constant pH (C1),
2. supports C2 and C3 resulting from an oxidation treatment of C1 with nitric acid 5 M in soxhlet for 3 and 6 h, respectively,
3. C4 obtained by adding C1 to a nitric acid 5 M solution and keeping the mixture at boiling temperature for 6 h,
4. C5 was prepared by oxidizing C1 with 5% O₂/N₂ at 723 K for 10 h;

5. C6 was obtained by removing the oxygen surface groups of C5 under N₂ flow at 1273 K. The sample was cooled immediately after reaching such temperature.

The supports were characterized for their texture and surface chemistry properties by nitrogen adsorption and temperature-programmed decomposition (TPD) and X-ray photoelectron spectroscopy (XPS), respectively.

The nitrogen adsorption isotherms were obtained at 77 K in a Coulter Omnisorp 100CX equipment. The mesopore areas (S_{me}) were determined by the *t*-method using the standard isotherm for carbon materials proposed in the literature [16], and the micropore volumes (V_0) were calculated by the Dubinin–Radushkevich equation.

The surface functional groups were qualitatively and quantitatively determined in an apparatus described elsewhere [17]. A SPECTRAMASS Dataquad quadrupole mass spectrometer was used to monitor the evolution of CO and CO₂ proceeding from the decomposition of the surface groups. The temperature was raised linearly up to 1373 K at 5 K/min under a helium flow (25 ml/min).

The oxygen surface groups were also analyzed by XPS in a VG Scientific ESCALAB 200A spectrometer using a non-monochromatized Mg K α radiation (1253.6 eV). Quantification was carried out using the O 1s sensitivity factor (2.850) [18]. The high-resolution spectra for O 1s were evaluated by deconvoluting the peaks using mixed Lorentzian–Gaussian functions. The distinct surface groups were identified according to the different oxygen binding energies as stated in the literature [19,20]. The groups and their corresponding binding energy are shown in Fig. 1. The width at half-height was fixed at 2.0 eV, and the peak center was allowed to vary within ± 0.2 eV.

2.2. Catalysts

The catalysts were prepared by impregnation using aqueous solution of hydrated hexachloroplatinic acid as the metal precursor. After 12 h, the excess solvent was removed by filtration and the catalysts were dried overnight at 383 K. The metal content is expected to be different as the carbon surface was chemically modified disturbing their adsorption capacity. The

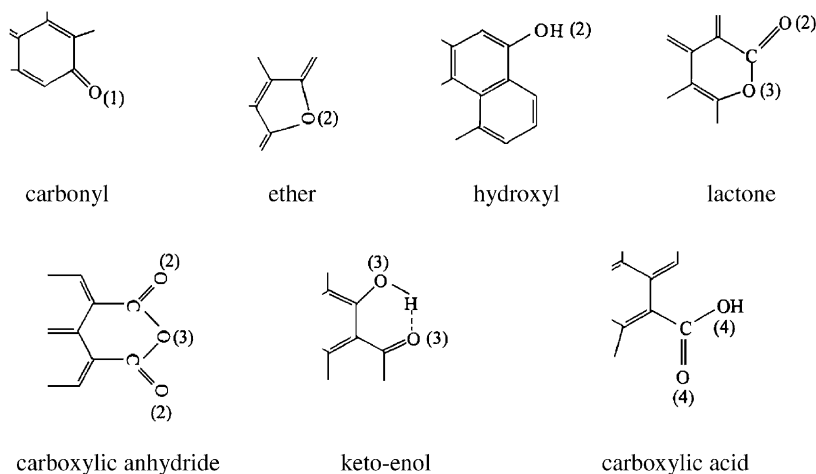


Fig. 1. Oxygen atoms in the carbon functional groups and their corresponding binding energy: group (1), 531.1 eV; group (2), 532.3 eV; group (3), 533.3 eV; group (4), 534.2 eV.

catalysts are named according to their parent support, e.g. Pt/C1.

The platinum load was determined by UV–Vis spectroscopy ($\lambda = 261.8$ nm) after burning away the support and dissolving the ash in aqua regia.

The platinum surface area was calculated by hydrogen chemisorption at 308 K, assuming the stoichiometry H:Pt = 1. The measurements were carried out in a Micromeritics ASAP 2000 equipment after an in situ reduction treatment under hydrogen at 673 K for 5 h.

The concentration of surface oxygen remaining after such reduction treatment was also investigated by XPS and is given as O/C ratio.

2.3. Enantioselective hydrogenation

The catalysts performance were evaluated in the liquid phase hydrogenation of methyl pyruvate using

(–)-cinchonidine as a chiral modifier. The reaction scheme is presented in Fig. 2.

Reactions were carried out in the same semibatch reactor currently used in our studies on selective hydrogenation [21–23]. The hydrogenations were carried out in ethanol at 313 K and 1 MPa with continuous addition of hydrogen. The experiments were conducted at 1400 rpm as it was seen to prevent hydrogen mass transfer and ensure kinetic control.

Before reaction, the catalysts were submitted to the same reduction treatment used before the hydrogen chemisorption measurements, i.e., under a hydrogen flow at 673 K for 5 h, and then transferred to the reactor. Next, the catalyst (0.1 g) was conditioned in situ for 1 h at 333 K and the final hydrogen pressure (1 MPa). The reactor was then cooled to the reaction temperature and 2 ml of methyl pyruvate and 50 mg of (–)-cinchonidine were injected after starting the

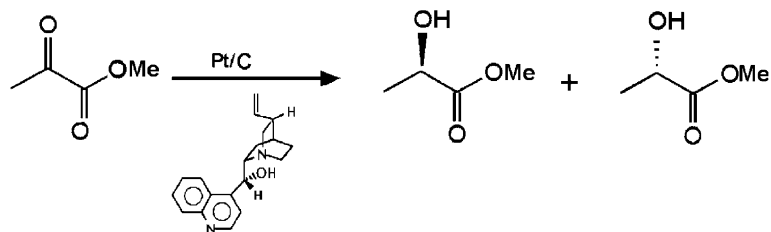


Fig. 2. Reaction scheme.

reaction. Both substrate and modifier were purchased from Aldrich.

Samples were taken periodically and analyzed by gas chromatography. Enantioselectivity was evaluated by the enantiomeric excess in (*R*)-methyl lactate. The initial reaction rate was derived from the pressure drop in relation to time; it is given as reactant uptake per second per platinum surface area ($\mu\text{mol s}^{-1} \text{m}^{-2}$).

3. Results and discussion

Table 1 collects the data obtained from the carbons nitrogen adsorption isotherms. It can be seen that all of them present similar textural properties, specially those oxidized in the liquid phase with HNO_3 (C1–C4). The mesopore area and micropore volume are affected when the support is treated with O_2 (C5). These changes are a consequence of the weight loss during oxidation with O_2 expressed as burn-off that, in this study, reached 13%. Exposing the carbon C5 at 1273 K (leading to carbon C6) does not further affect the support texture.

Regarding the surface chemistry, it is well known that different oxidation treatments lead to distinct oxygen surface groups [13,14,17]. The spectra displayed in Fig. 3a show that the liquid phase treatment (C2–C4) creates surface oxygen groups, which decomposes as CO_2 at low temperatures (between 400 and 800 K). It must be stressed, however, that a small amount of CO_2 in this temperature range is already detected with the starting material C1, which can be attributed to the oxygen adsorption from air during storage [24,25]. A peak at higher temperatures (~ 900 K) can be seen in the CO_2 spectrum of C5 and corresponds to more stable oxygen surface groups. The spectra of supports C5 and C6 reveal that the

thermal treatment efficiently removed the functional groups although their texture remained unchanged.

Comparing these spectra with the data available in the literature [17], one may identify the first CO_2 -type group (< 800 K) as carboxylic acid and the higher temperature CO_2 peak (800–1000 K) as carboxylic anhydrides and lactones.

The surface groups that originate CO in the TPD have been identified as weakly acidic functional groups such as phenols, carbonyls and quinones [17]. The CO spectra are exhibited in Fig. 3b. Although all carbons released CO upon heating, it can be noticed that such groups are preferentially created by the gas phase oxidation treatment. This trend is clearly illustrated by the values of CO/ CO_2 ratio obtained for the supports (Table 1), which decreases from C1 to C4 while a dramatic increase can be observed for C5. The ratio obtained for C6 is consistent with the one from non-oxidized carbon C1 and evidences the removal of the surface groups. Table 1 also lists the amounts of CO and CO_2 evolved from each support.

The use of XPS to characterize surface groups in carbon-based materials, especially of carbon fibers, has increased rapidly. The evaluation of oxygen surface groups is based on the deconvolution of the high-resolution spectra for O 1s according to the different oxygen binding energies as schematically represented in Fig. 1. Table 2 shows the oxygen atomic surface content for all supports. The oxygen surface content of the supports oxidized in the liquid phase increases with the severity of the oxidation. The absence of oxygen in the C5 sample at 534.2 eV, energy associated with carboxylic acid group, is in agreement with the results obtained by TPD and with the postulate that such group is not stable at the temperature used in the gas phase oxidative treatment.

Table 1
Textural and surface chemical properties of the carbons

Carbon	Oxidation treatment	S_{me} (m^2/g)	V_0 (cm^3/g)	CO (mmol/g/s)	CO_2 (mmol/g/s)	CO/ CO_2
C1	Commercial carbon	122	0.441	0.570	0.126	4.52
C2	5M HNO_3 in soxhlet for 3 h	128	0.448	1.082	0.380	2.85
C3	5M HNO_3 in soxhlet for 6 h	125	0.454	2.253	1.099	2.05
C4	5M HNO_3 for 6 h	116	0.405	4.292	2.576	1.67
C5	5% O_2/N_2 at 723 K for 10 h	143	0.580	3.036	0.248	12.24
C6	C5 exposed at 1273 K under N_2	140	0.593	0.520	0.099	5.25

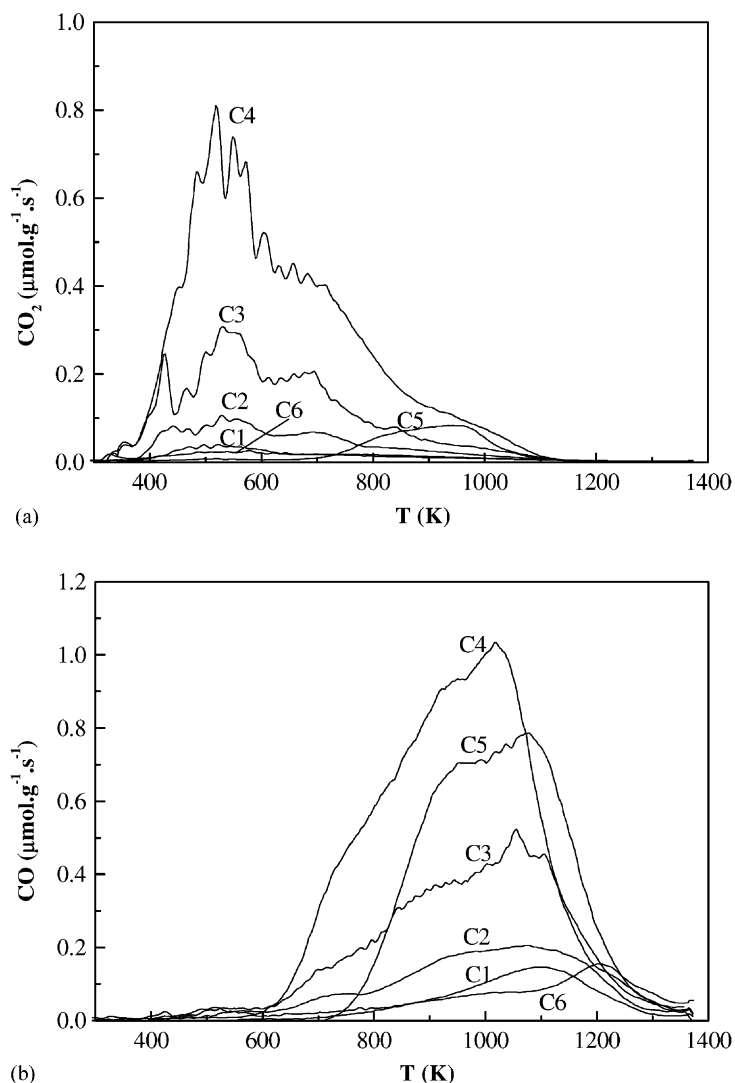


Fig. 3. TPD spectra of: (a) CO₂ and (b) CO evolved from the carbons.

Table 2

Oxygen surface composition of the supports

Support	Oxygen surface composition (%)			
	531.1 (eV)	532.3 (eV)	533.3 (eV)	534.2 (eV)
C1	1.263	2.852	2.019	1.537
C2	2.063	3.928	3.067	1.969
C3	2.567	5.010	4.108	2.608
C4	3.034	7.471	6.771	3.972
C5	2.830	2.777	3.717	–
C6	0.723	1.949	1.182	0.884

The nature and the concentration of surface groups on the supports are expected to influence the adsorption process of the noble metal precursor ions during impregnation. Accordingly, the results displayed in Table 3 reveal that the more oxidized is the support, the lower is the metal content of the catalyst after impregnation. It was also found that the oxygen surface groups have a negative effect on dispersion translated in Table 3 as the platinum surface area.

The catalysts performances were evaluated in terms of activity and enantioselectivity, which are

Table 3
Catalysts characteristics and their catalytic performance

Catalyst	Pt (%)	S_{Pt} (m ² /g)	r_0 (μmol/s/m ²)	ee (%)
Pt/C1	5.74	105	0.62	29
Pt/C2	5.46	57	1.34	30
Pt/C3	4.64	27	4.72	31
Pt/C4	2.57	7	9.34	35
Pt/C5	5.84	25	9.05	33
Pt/C6	4.64	62	1.18	34

presented and compared in Figs. 4 and 5, respectively.

Differences in the catalysts behavior can be clearly seen, especially in the catalytic activity that is particularly affected. Enantioselectivity, on the other hand, is revealed to be independent of the catalysts features and is around 30% for all systems. Such performances should be analyzed based on the type and extension of the oxidizing treatment applied

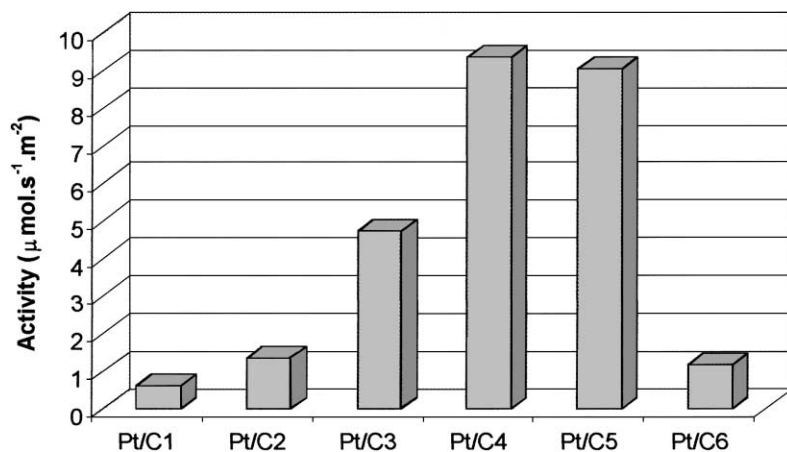


Fig. 4. Catalytic activity of Pt/C catalysts in the enantioselective hydrogenation of methyl pyruvate.

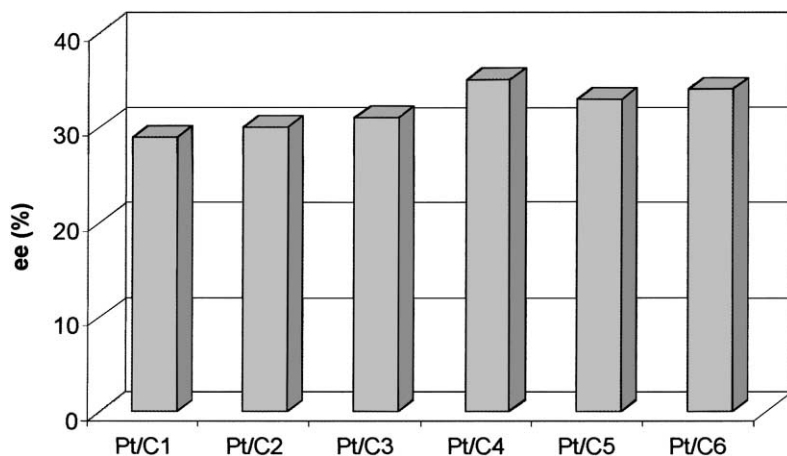


Fig. 5. Enantiomeric excess in (*R*)-methyl lactate achieved with each catalyst.

to the supports as it is the basic difference in the samples.

Comparing the activity of the first four samples (Pt/C1–Pt/C4), which were prepared on carbons oxidized in the liquid phase and which present the same textural properties, it can be observed that the more oxidized is the carbon the more active is the parent catalyst. The oxidation degree may be taken as the total amount of CO and CO₂ released by the supports and detected by TPD (Table 1).

Conversely, the performance of Pt/C5 is rather comparable to the Pt/C4 even though it is less oxidized. In fact, Pt/C5 performance should be faced with Pt/C3 due to its similar characteristics (Table 1), and such results could suggest an influence of the chemical nature of the surface groups. However, it must be outlined that some functional groups are not stable at high temperatures as shown by TPD experiments. Decomposition occurs under either inert or reductive atmosphere though the profiles are slightly different [26]. Therefore, to avoid a misleading conclusion and for better evaluation of such an influence, the catalytic activity must be correlated to the content of surface oxygen remaining after the reduction step. In this work, the reduced catalysts were analyzed by XPS and the surface oxygen content is given by the O/C ratio.

As shown in Fig. 6, the influence on activity indeed seems to be brought about by the remaining oxygen in the carbon surface. Despite the equivalent degree of oxidation achieved over the supports C3 and C5, the groups formed in the gas phase (C5) are thermally

more stable than those created in the liquid phase oxidation (C3). Accordingly, the content of surface oxygen after reduction at 673 K is expected to be higher for Pt/C5 spectra (Fig. 3). This observation suggests that such surface groups remaining after activation act by increasing the carbon hydrophilicity thus enabling the reactants to go through the catalyst and improving its activity.

It can be inferred therefore that differences in the chemical nature of the surface functional groups do not directly influence the catalytic activity. The performance of the catalyst Pt/C6 also provides supporting evidences. Its textural properties are the same as the Pt/C5 as their supports were submitted to the same treatment and reached the same burn-off. Nevertheless, the thermal treatment under N₂ at 1273 K efficiently removed all the functional groups and, therefore, its activity is seen to decrease. Its performance is in close agreement with those from the non-oxidized or less oxidized samples (Pt/C1 and Pt/C2) listed in Table 3.

In addition to the increase in hydrophilicity, we can also question the role played by the surface functional groups in the activation of the methyl pyruvate C=O bond. The thermal decomposition of surface groups upon activation creates active sites capable of chemisorbing hydrogen following the steps proposed for the process of carbon gasification with hydrogen to methane formation [27]. In this mechanism, the hydrogen chemisorbed on such active sites generates –CH₂ species, which are subsequently hydrogenated to –CH₄ and, lastly, desorbed as methane,

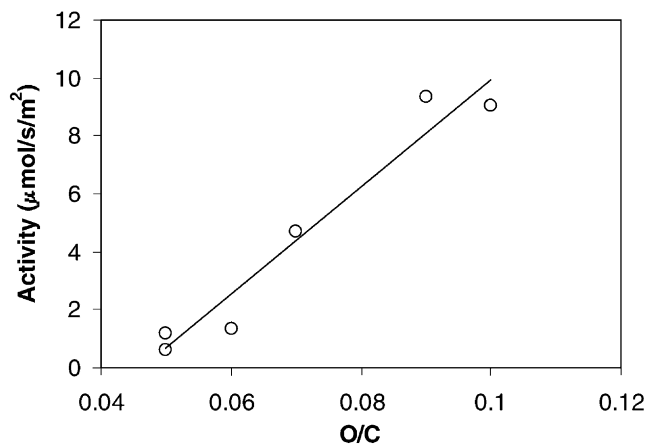


Fig. 6. Correlation between catalytic activity and the surface oxygen concentration on the catalysts after activation procedure.

allowing the reaction to proceed continuously on the free sites. The platinum presence on carbon makes hydrogen chemisorption easier as the hydrogen dissociatively chemisorbed on the metal may be transferred to the support via spillover mechanism. It can then react with the active sites generated by decomposition [24,28]. Such hydrogen species present on the support and near the metallic sites can polarize the substrate carbonyl group through hydrogen bond interaction with the oxygen atom from the C=O bond. This interaction would weaken the carbonyl bond and facilitate the hydrogenation. According to this mechanism, we can expect that the higher the surface groups concentration, the higher will be the formation of active sites for hydrogen chemisorption on the support and, therefore, the higher will be the catalytic activity. The results obtained in this work indeed follow such a trend. This C=O polarization mechanism has been accepted to explain the increase in selectivity towards unsaturated alcohols in the hydrogenation of α,β -unsaturated aldehydes over monometallic catalysts supported on carbon [12].

Regarding enantioselectivity, one could expect some support effect, especially from carbon characterized by the presence of surface groups such as lactones, quinones and carbonyls. The interaction between the substrate carbonyl group and the nitrogen atom in modifier quinuclidine ring could be somewhat disturbed by the competing surface carbonyl groups. Such a behavior was indeed observed by Farkas et al. [8] for Pd based catalysts used in C=C asymmetric hydrogenation. Nevertheless, in this work we could not verify any influence. The ability of Pt/C catalysts to accommodate the appropriate conformation of the reactant–chiral modifier complex does not seem to be disturbed either by the nature or the amount of surface oxygen groups.

4. Conclusions

The oxidation treatments applied to the activated carbon influence the catalysts performance. The behavior of the different Pt/C samples revealed that the catalysts prepared on oxidized supports are more active. The higher activity is associated with the concentration of surface oxygen remaining after activation. Such remaining oxygen increases the catalyst

hydrophilicity facilitating the reactants transport. A hydrogen bond interaction between the oxygen atom from the substrate C=O bond and the hydrogen species chemisorbed on the support is also suggested to be responsible for the catalysts activity. The chemisorbed hydrogen species are located on the active sites created after the thermal decomposition of the surface groups. Enantioselectivity did not seem to be affected either by the surface content or by the chemical nature of the functional groups.

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