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Chemoselective Pt-catalysts supported on carbon-TiO₂ composites for the direct hydrogenation of citral to unsaturated alcohols

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ABSTRACT

A series of carbon xerogels-TiO₂ composites with different TiO₂ contents were prepared, exhaustively characterized and used as a Pt-support to develop selective hydrogenation catalysts. The carbon phase in the composite hinders the TiO₂ crystal growth and the transformation to rutile during thermal treatments. Textural, chemical and catalytic properties are determined by the TiO₂ content, with an optimum around 40 wt.% of TiO₂ content. The mesoporosity of the supports, the Pt-dispersion and Pt-support interactions are favoured in this sense. During the H₂-pretreatment, the Pt and TiO₂ phases were simultaneously reduced and the formation of oxygen vacancies leads to the mobility of Pt-species inside the TiO₂ structure, avoiding sintering in surface and strongly improving both catalytic activity and selectivity. The catalytic performance was discussed on the basis of the sample characteristics. Unsaturated alcohols were obtained as main reaction products in all cases, being the only product in the case of the optimized catalyst.

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1. Introduction

Nowadays, unsaturated alcohols (UA) are highly demanded by organic synthesis, fine chemistry, perfumery or pharmaceutical industries [1,2]. These compounds can be obtained from available α . β -unsaturated aldehvdes. Among them, citral (3.7-dimethyl-2,6-octadienal) is a cheap raw material which is one of the main components of the lemongrass oil and it can also be produced at a large scale trough petrochemical processes [3]. Valuable UA, nerol and geraniol, can be obtained from citral. However, citral is a multi-unsaturated compound containing both an isolated double bond (C=C) and another C=C conjugated to a carbonyl (-C=O) group [4,5]. Consequently, the citral hydrogenation presents a complex reaction scheme [6] leading to a variety of products. The main problem is that the hydrogenation of C=C bonds is thermodynamically favoured over the C=O bonds; moreover, there is also a series of side reactions such as acetalization, cyclization or cracking [4,7,8] that reduces the UA yield.

To obtain the chemoselective C=O hydrogenation, specific catalysts should be designed [8–10]. The use of monometallic heterogeneous catalysts, instead of forming UA, leads mainly to unsaturated aldehyde (citronellal) or saturated alcohol (3,7 dimethyl octanol) due to the hydrogenation of the C=C bonds

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http://dx.doi.org/10.1016/j.jcat.2016.09.026 0021-9517/© 2016 Elsevier Inc. All rights reserved. [11,12]. The catalytic performance is influenced by the active phase, the support nature and their interactions. Probably, the most important parameter is the selection of the active phase. This factor has been studied by different authors [13–16], and Vannice and Singh [16] show that the catalytic activity in citral hydrogenation varies as Pd > Pt > Ir > Os > Ru > Rh > Ni > Co \gg Fe. Nevertheless, the selectivity to UA of these monometallic catalysts is high only for Os-catalyst (at around 88%), moderate for Ru and Co (55%) and null (0% UA) being selective to citronellal, for Pt, Ir, Rh, Ni and Pd-catalysts.

This performance however, strongly depends on the support, as revealed by different studies [17,18]. Therefore, by studying the influence of the supports (graphite, KL zeolite and ZrO₂) on Rucatalyst performance [17], it was pointed out that using graphite as Ru-support, the selectivity to UA is favoured by electronic transfers from graphite to the Ru-particles with the formation of electron-rich metal species. In the case of Ru-supported on ZrO₂, this effect is associated with the formation of Ru⁰-Zrⁿ⁺ species and when supported on KL zeolite the hydrogenation of the carbonyl group and poisoning resistance are favoured by geometrical factors (pore characteristics and localization of the Ru-particles). Ru/KL is the most selective catalyst to UA (around 50%), but it is poorly active.

In previous works [13,19] we also pointed out the influence of the chemical and porous characteristics of both carbon and inorganic supports used to develop Pt-catalysts for citral

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hydrogenation. Using carbon supports, the performance of the derivatives Pt-catalysts strongly depends on the micro/mesoporous character of this support and the presence of impurities, namely inorganic components. Mesoporosity and acid impurities leads to a decrease in UA yields; therefore, the best results were obtained with pure microporous carbon xerogels [19]. Similar conclusions were obtained when using inorganic supports: mesoporosity favours secondary reactions inside the pores, while Brönsted acidity strongly favours cracking reactions [13]. On such a basis, Al_2O_3 always provides worse results than TiO₂ as Pt-supported catalysts for citral hydrogenation, in spite of their similar porous characteristics and pH_{pzc} values.

This behaviour also highly depends on the pretreatment conditions of the catalyst, which determine the chemical and crystalline transformation of the supports as well as the nature and dispersion of the active phase. In spite of the fact that Pt-sintering in general is favoured by H₂-pretreatment regarding the He-pretreatment [20] (which should lead to a stronger catalyst deactivation) using Pt/ TiO₂ catalysts, its catalytic performance is improved after the H₂pretreatment. This is because the H₂ treatment also favours the partial reduction of the TiO₂ surface in such a way that the synergetic combination of Pt site/oxygen vacancy, strongly favours the C=O hydrogenation to UA during citral hydrogenation [21].

These results show new opportunities in the preparation of highly selective hydrogenation catalysts by optimizing the support characteristics and the interactions with the corresponding active phase. New Pt-supports can be developed by taking advantage of the ability of TiO₂ to produce specific active site for citral adsorption through the C=O bond, the developed porosity and fitted surface chemistry (basicity) of pure carbon xerogels. The sol-gel synthesis procedure guarantees the purity of these supports avoiding interferences of the mineral matter present on classical activated carbons. The high surface area of carbon xerogels should facilitate the distribution and reduction in the titanium dioxide particles in the composite, as well as the Pt-dispersion favouring the metal-support interactions (SMSI effect) in the derivative catalysts. So that, in this work, TiO₂-carbon xerogel composites are prepared with different TiO₂ percentages and used as supports to develop specific and chemoselective Pt-catalysts for citral hydrogenation reactions. The catalytic behaviour of these samples was studied, relating activity and mainly selectivity to their chemical, structural and porous characteristics.

2. Experimental

2.1. Synthesis of TiO₂-carbon xerogel composites

Carbon-TiO₂ composites were prepared by the sol-gel synthesis procedure using resorcinol-formaldehyde and titanium isopropoxide (IV) as carbon and TiO₂ precursor, respectively. In a typical synthesis procedure, Span 80 (S) was dissolved in 900 ml of n-heptane and heated at 70 °C under reflux and stirring (450 rpm). After stabilizing this temperature, another aqueous (W) solution containing the corresponding amount of resorcinol (R) and formaldehyde (F) was added drop-wise. The organic RF gel was formed immediately and after that, the proper amount of titanium isopropoxide was also added drop by drop to the suspension. The final molar ratio of the mixture was R/F = 1/2, R/W = 1/14 and R/S = 4.5.

The formed hydrogel was aged at 70 °C for 24 h under stirring after which the solid, displaying an intense orange colour, was recovered by filtering and placed in acetone for 5 days (changing acetone twice daily) to remove the rest of unreacted products and to exchange solvents within the pores by acetone. This procedure reduces the collapse of porosity during the subsequent drying process [22]. Then, the gel was filtered again and dried by micro-

wave heating under an argon atmosphere in periods of 1 min at 300 W until constant weight, using a Saivod MS-287W microwave oven. The pyrolysis of organic xerogel-titanium oxide composites to obtain the corresponding carbon-TiO₂ composites, was carried out at 900 °C in a tubular furnace using a N₂ flow at 300 cm³/ min and a heating rate of 1 °C/min, in order to allow a soft removing of pyrolysis gases, and a soaking time of 2 h at this temperature.

The recipes were fitted to obtain six carbon-TiO₂ composites containing a different amount of titanium oxide (around 10, 20, 30, 40, 50 and 80 weight% in the carbonized materials). For that, the proportion of organic and inorganic precursor was balanced and a weight loss during carbonization of around 50% was assumed according to previous experiences. The real TiO₂ content of the samples was finally determined by thermogravimetric analysis (TGA) using a Mettler-Toledo TGA/DSC1 thermobalance and burning the organic fraction at 500 °C in flowing air until constant weight. Carbon-TiO₂ composites were refereed as CTiX (X corresponding to the theoretical TiO₂ content programmed for each sample, e.g. CTi40 should contain around 40 wt.% of TiO₂). Additionally, a pure carbon xerogel prepared in our laboratories [13,19] and titanium dioxide (anatase, from Alfa Aesar) were used as reference materials.

2.2. Catalysts preparation

All supports were milled and sieved to a diameter smaller than 0.15 mm before impregnation. Platinum catalysts were prepared by impregnation at 3 wt.% Pt-loading using an aqueous solution containing the appropriate amount of $[Pt(NH_3)_4]Cl_2$, dried over night at 120 °C and finally pretreated in H₂ flow at 400 °C (heating rate of 5 °C/min) for 12 h. Catalysts were refereed indicating the support, the Pt-content and the final mean Pt-particle size determined by H₂-chemisorption. Therefore, as an example, CTi40Pt3-9 indicates that Pt nanoparticles present a mean particle size of 9 nm when deposited with a 3 wt.% Pt-loading on the carbon-TiO₂ composite which contains 40% of titanium oxide.

2.3. Textural and chemical characterization

Textural characterization was carried out by N₂ and CO₂ adsorption at -196 °C and 0 °C, respectively, using a Quantachrome Autosorb-1 equipment. The BET and Dubinin–Radushkevich equations were applied to determine the apparent surface area (S_{BET}) and the micropore volume (W_0), the mean micropore width (L_0) and the microporous surface (S_{mic}), respectively. Furthermore, the BJH method was used to calculate the mesopore volume of the samples (V_{mes}). Pore size distributions were also obtained by applying the BJH method. The total pore volume was considered as the volume of N₂ adsorbed at $P/P_0 = 0.95$.

The titania phase was determined by a powder X-ray diffraction (XRD) pattern, using a Bruker D8 Advance X-ray diffractometer with Cu K α radiation at a wavelength (λ) of 1.541 Å. The 2 θ angles were scanned from 20° to 70° and the average crystallite sizes (D) were estimated by the Debye-Scherer equation.

Pt dispersion (D) and mean particle size (d) were obtained by H₂-chemisorption and high-resolution transmission electron microscopy (HRTEM). The H₂-chemisorption isotherms were measured at 25 °C. The Pt dispersion (D) is obtained from the amount of H₂-chemisorbed assuming a stoichiometric ratio H₂:Pt = 1:2 (dissociative chemisorption) and the average particle size was calculated as $d_{Pt}(H_2) = 1.08/D$ (nm). The chemical characterization of the catalysts was further analysed by X-ray photoelectron spectroscopy (XPS). The spectra were obtained on a Kratos Axis Ultra-DLD X-ray photoelectron spectrometer equipped with a hemi-

spherical electron analyzer connected to a detector DLD (delay-line detector).

2.4. Catalytic performance

The citral hydrogenation was carried out in 100 ml heptane solution at a constant hydrogen pressure of 8.3 bar and 90 °C using a Parr reactor model 5500. The experimental conditions such as citral concentration, catalyst weight and stirring speed, were previously optimized in order to avoid mass transfer limitations (results not showed) and fixed in 0.05 M, 500 mg and 1500 rpm, respectively. A small volume of the sample (1 mL) was periodically withdrawn and analysed by chromatography using a Bruker 430-GC equipped with a FID detector and a Varian GC Capillary Column CP7485 (25 m \times 0.32 mm \times 0.45 µm). Citral and all possible products were previously calibrated.

3. Results and discussion

3.1. Support characterization

The TiO₂ content, present in each composite and determined by TGA is shown in Table 1. The TiO₂ percentages are slightly higher than the theoretical ones, due to the weight lost during the carbonization which is not exactly 50%; however, the experimental data are much closer to the expected ones. The pH_{pzc} values point out the different acid-base characteristics of each support. Because pure carbon material is a basic support while pure TiO₂ phase is acid, in general the pH_{pzc} values tend to decrease when increasing the TiO₂ content in the composite.

Powder XRD measurements of carbon-TiO₂ composites were performed in order to determine the nature and particle size of TiO₂ (Fig. 1). Below a TiO₂ content of 30%: XRD patterns do not show any defined diffraction peak corresponding to the inorganic phase, the small shoulders observed are characteristic of the amorphous carbon component, indicating a very small nanoparticle size or the amorphous character of the TiO_2 phase. With a greater TiO_2 content, crystallinity of the samples increases and wide peaks corresponding to the anatase polymorphic form, are observed in the CTi40 XRD pattern. An incipient rutile phase is observed on CTi50, being rutile however predominant only in the composite CTi80. For pure TiO₂ oxide (patterns not included) this transformation is fast at temperatures above 730 °C, but the phase transition temperature has been shown to depend on impurity content, particle size and surface area [23]. The above results even after carbonization at 900 °C indicate the following: the low crystallinity of TiO₂ in the composites denotes that this phase is mainly well dispersed on the carbon phase, which prevents the sintering of TiO₂ nanoparticles and stabilizes the anatase structure at high temperature when TiO₂ content is smaller than 50 wt.% (i.e. avoiding the rutile formation).

The pore structure of the composites was analysed by comparing the results from CO_2 and N_2 -adsorption experiments. Results

Table 1	
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composition, composition propping of competition	Composition,	TiO_2 c	rystal	size	and	pH _{pzc}	of	supports.
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Sample	TiO ₂ (wt.%)	Crystal size (DRX)	pH_{pzc}
Carbon	0	-	9.4
CTi10	15	-	7.9
CTi20	22	-	7.8
CTi30	34	3.4	7.3
CTi40	45	4.3	7.1
CTi50	54	6.7	7.0
CTi80	84	8.0	6.4
TiO ₂	100	24.6	4.9



Fig. 1. Powder XRD patterns of samples: CTi10 (\triangle), CTi20 (\diamond), CTi30 (\Box), CTi40 (\bigcirc), CTi50 (∇) and CTi80 (\Box). Anatasa (\blacksquare), Rutile (\blacktriangle).

are collected in Table 2. It is well known that the CO₂ adsorption provides the information about the narrow microporosity, corresponding to micropores with a diameter lower than 0.7 nm, while the total microporosity is obtained from N₂ isotherm only in the absence of diffusion restrictions [24]. The results obtained from CO₂ and N₂ adsorption show a great variation between the textural properties of the composites. This fact is due to the different porosity ranges also present in both pure phases. Therefore, the pure carbon phase is typically a microporous material that presents a high surface area value. The narrow porosity is predominant, as indicated by the fact that $S_{\text{mic}} \gg S_{\text{BET}}$, which points out the diffusional restrictions of N2 molecules to the interior of the narrowest microporosity. However, the TiO₂ phase presents smaller surface area values but a significantly higher mesoporosity (V_{mes}). Therefore, the microporosity is progressively widening when increasing the TiO_2 content, the volume of narrow micropores (W₀ (CO₂)) progressively decreases and the mean micropore size $(L_0 (CO_2))$ remains practically constant at around 0.6 nm in all the composites (as in the carbon support), although $(L_0 (N_2))$ progressively increases.

The mesopore size distribution (PSD) for the composites, obtained by the application of the BJH method to the corresponding N₂-adsorption isotherms, is shown in Fig. 2a. It is noteworthy that samples with TiO₂ content between 20 and 40% present a main maximum for mesopores at around 16.8 nm. The composites with smaller (CTi10) or higher (CTi80) TiO₂-content present a PSD with the corresponding maxima shifted to smaller pores. Increasing the% TiO₂, the total porosity (V_{0.95}) of the composites is favoured (Table 2) which is mainly induced by the development of mesoporosity (Fig. 2a and b), but this strongly decreases at a high TiO₂ content (CTi80), probably also induced by the rutile formation.

Therefore, the mesopore volume increases more or less linearly with the TiO₂ content (up to CTi50, Fig. 2b) while the micropore volume (determined by N₂ or CO₂ adsorption) shows the opposite tendency (Fig. 2c and d). In this sense, the micropore size (L_0) also

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Table 2

Textural characteristics of supports.

Carbon	$S_{\rm BET} ({ m m}^2{ m g}^{-1})$	$W_0 (N_2) (cm^3 g^{-1})$	$W_0 (CO_2) (cm^3 g^{-1})$	$L_{0}\left(\mathrm{N}_{2} ight) \left(\mathrm{nm} ight)$	L_0 (CO ₂) (nm)	$V_{\rm mes}({\rm cm}^3{\rm g}^{-1})$	$S_{\rm mic} ({\rm CO}_2) ({\rm m}^2 {\rm g}^{-1})$	$V_{0.95} ({\rm cm}^3{\rm g}^{-1})$
С	614	0.245	0.285	0.78	0.60	0.060	952	0.305
CTi10	523	0.206	0.223	0.87	0.58	0.116	768	0.322
CTi20	480	0.190	0.205	0.76	0.56	0.203	737	0.393
CTi30	481	0.192	0.176	0.97	0.58	0.242	608	0.434
CTi40	586	0.227	0.174	1.21	0.62	0.438	562	0.665
CTi50	507	0.163	0.144	1.22	0.61	0.392	473	0.555
CTi80	176	0.070	0.057	1.20	0.62	0.081	185	0.151
Ti	116	0.047	0.054	1.89	0.68	0.272	159	0.326



Fig. 2. (a) Pore size distribution of supports: CTi10 (△), CTi20 (◊), CTi30 (□), CTi40 (◊) and CTi80 (◊) and evolution of the corresponding pore volumes (b) V_{meso}, (c) W₀ (CO₂) and (d) W₀ (N₂) with TiO₂ content.

progressively increases and consequently, with the micropore widening, the commented diffusional restriction decreases and therefore also the difference between the S_{mic} and S_{BET} values.

Pretreated catalysts were also characterized before reaction, following the same procedure previously described for the supports. Textural properties and pH_{pzc} are summarized in Table 3. All the pretreated catalysts present a smaller pH_{pzc} value than their respective supports; nevertheless, these values also slowly decrease when increasing the TiO₂ content.

It is also noteworthy that the surface values of the catalysts are significantly smaller than those of their corresponding supports. These results are obviously a consequence of the partial blockage of the support porosity by the Pt-nanoparticles, as denoted by the decrease in both micropore (W_0 (N₂)) and mesopore (V_{mes}) volumes. Nevertheless, these differences strongly decrease when increasing the TiO₂ content of the composite (Table 3), in such a way that the N₂-adsorption isotherms of supports and catalysts are quite coincident for TiO₂ contents greater than 20% (Fig. 3).

Table 3

Textural characteristics and	pHpzc of	pretreated	catalysts
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Catalyst	$S_{\rm BET} (m^2 { m g}^{-1})$	W_0 (N ₂) (cm ³ g ⁻¹)	$L_{0}(N_{2})(nm)$	$V_{\rm mes}~({\rm cm}^3{\rm g}^{-1})$	$V_{0.95} ({\rm cm}^3{\rm g}^{-1})$	pH_{pzc}
CPt3	531	0.21	0.62	0.000	0.220	8.8
CTi10Pt3	315	0.123	1.21	0.077	0.200	5.9
CTi20Pt3	359	0.144	0.95	0.146	0.290	5.8
CTi30Pt3	352	0.140	1.23	0.300	0.440	5.7
CTi40Pt3	483	0.193	1.33	0.427	0.620	5.6
CTi50Pt3	533	0.212	1.42	0.355	0.567	5.5
CTi80Pt3	154	0.062	1.51	0.107	0.169	4.9
TiPt3	111	0.045	1.62	0.397	0.442	3.6

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Fig. 3. Nitrogen adsorption-desorption isotherms. 🔺 CTiX, 🔶 CTiXPt3. Open symbols: desorption, closed symbols: Adsorption.

Clearly, microporosity is preferentially blocked by the metallic nanoparticles: L_0 (N₂) increases while W_0 (N₂) decreases. These results suggest that Pt-nanoparticles are mainly located on the largest micropores and mesopores of the composite, blocking the narrowest micropores from the carbon phase. Therefore, when using composites with a high TiO₂ content (>40%), similar PSD is obtained regarding their supports (Fig. 3), due to the low proportion of micropores in these samples.

The Pt-dispersion of pretreated catalysts was analysed by H_2 chemisorption, XRD and HRTEM. Results are summarized in Table 4. Nevertheless, the results should be carefully analysed because different tendencies can be described. Previous studies [25] showed that the mesopore volume of the support contributes to a higher Pt-dispersion. However, in this case, according to the H_2 -chemisorption data, dispersion does not improve by increasing the mesopore volume of the supports. On the contrary, even a slight but progressive increase is observed of the Pt-particle size when increasing the percentage of TiO₂.

However, XRD seems to indicate that smaller particles are formed when increasing the TiO_2 content. When comparing the XRD patterns of pretreated catalysts at 400 °C (Fig. 4), a decrease in the intensity of the main Pt [111] diffraction peak is observed, increasing the % of titania in the composite from 10 to 30% above which no diffraction peaks (corresponding to the Pt-phase) are observed. The observed improved Pt-dispersion could be related, as commented, with the higher mesopore volume of the supports. Nevertheless, the Pt-diffraction peaks were not observed when using the composite CTi80 or pure TiO_2 supports, which have a low mesopore volume. Therefore, the different textural properties do not explain this effect.

Equally, when increasing the pre-treatment temperature of TiC20Pt3 catalysts to 450 °C, an increase in Pt XRD peaks was also

Table 4

Mean Pt-particle size determined for pretreated catalysts by H₂ chemisorption (\overline{d}_{H_2}), XRD or HRTEM.

Catalyst	Q_{H_2} (µmol/g)	\overline{d}_{H_2} (nm)	\overline{d}_{XRD} (nm)	\overline{d}_{HRTEM} (nm)
CPt3-8	10.5	7.9	9.3	8.2
CTi10Pt3-7	12.8	6.5	25.3	5.1
CTi20Pt3-7	12.0	6.9	11.3	4.5
CTi30Pt3-9	9.0	9.2	4.9	-
CTi40Pt3-9	8.9	9.3	n.d.	1.3
CTi50Pt3-10	8.5	9.7	n.d.	-
CTi80Pt3-10	8.1	10.3	n.d.	1.6
CTi20Pt3-11 ^a	7.7	10.7	5.6	2.2
TiPt3-9	9.0	9.2	n.d.	3.6

(n.d.) no XRD peaks detected.

^a After pretreatment at 450 °C.

expected, because increasing the temperature should favour sintering as observed by H_2 -chemisorption. However, again, a decrease in the intensity of the Pt [111] diffraction peak is clearly observed regarding the same sample pretreated at 400 °C (Fig. 5), therefore leading to a smaller Pt-particle size value determined by the Scherrer equation.

In order to clarify the controversy between XRD and chemisorption results, samples were also analysed by HRTEM (Fig. 6). This technique confirms a higher Pt-dispersion (smaller Pt-particle size) increasing the amount of TiO_2 in the carbon composite materials (Fig. 6a and b). Small Pt-nanoparticles of around 2 nm were detected at high TiO_2 loadings. Ti and Pt distributions were analysed by EDX and the corresponding mapping (Fig. 6c and d) shows that Ti is presented along the complete composite surface while Pt is forming nanoparticles, although these nanoparticles are also homogeneously distributed. The size of these Pt-nanoparticles is higher on the CTi10 than on CTi40 or CTi80 composites.

A previous work [21] pointed out the formation of 3-D and crystalline Pt-particles on Pt/TiO₂ catalysts after He-pretreatment. However, Pt-XRD peaks were not observed after H₂-pretreatment at the same temperature. This fact was justified because the reductive character of the H₂-atmosphere simultaneously induces the partial reduction of the TiO₂ phase and the formed oxygen vacancies favour the mobility of Pt-species into the TiO₂ structure. This



Fig. 4. Influence of the TiO₂ content on the XRD-patterns of catalysts pretreated at 400 °C: CTi10Pt3-7 (Δ), CTi20Pt3-7 (\diamond), CTi30Pt3-9 (\Box), CTi40Pt3-9 (\bigcirc), CTi50Pt3-10 (\neg), CTi80Pt3-10 (\rightarrow), TiPt3-9 (\blacksquare).

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Fig. 5. Influence of the pretreatment temperature on the XRD-patterns of CTi20Pt3 catalyst. 400 (\diamond) 450 °C (\blacklozenge).

fact avoids sintering on the support surface and the formation of 3-D crystallites that could be observed by XRD, but simultaneously also decreases the Pt-concentration on the surface, therefore decreasing the amount of H₂-chemisorbed during the characterization experiments.

A similar effect is observed in the present catalyst series. Using composites with low TiO_2 -content as supports, 3D and crystalline Pt-particles are observed by XRD or HRTEM. They are formed mainly on the predominant carbon phase, as denoted by the textural and Pt-dispersion analysis. When increasing the TiO_2 loading above 20–30%, the formation of small Pt particles is favoured. In addition, the vacancies concentration and the mobility of the Ptspecies increase with the TiO_2 content and the pre-treatment temperature, favouring the progressive migration of Pt species into the TiO_2 structure. This fact reduces the H₂-chemisorption capacity of the samples, leading to a false increase in the Pt-particle size values determined by this technique, in spite of the fact that smaller particles are formed.

The surface chemistry of pretreated catalysts was analysed by XPS. Results are collected in Table 5 and Fig. 7. Three components



Fig. 6. HRTEM images of (a) CTi10Pt3-7, (b) CTi80Pt3-10 and EDX mapping, (c) CTi10Pt3-7 and (d) CTi40Pt3-9.

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5	Table 5	
]	Pt-surface concentration and distribution of Pt-species determined by XPS	

Catalyst	BE (eV) Pt ⁰	Pt (0) (%)	BE (eV) Pt ²⁺	Pt (II) (%)	Pt _{XPS} (wt.%)	O _{XPS} (wt.%)	C _{XPS} (wt.%)	Ti _{XPS} (wt.%)
CPt3-8	71.3	70	72.3	30	4.38	2.54	93.08	0.00
CTi10Pt3-7	71.6	67	72.5	33	1.71	3.80	93.30	1.19
CTi20Pt3-7	71.5	67	72.5	33	1.39	3.99	92.06	2.56
CTi20Pt3-11	71.6	72	72.6	28	1.61	5.92	81.78	10.69
CTi30Pt3-9	71.6	70	72.7	30	1.19	5.86	83.57	9.38
CTi40Pt3-9	71.6	70	72.7	30	1.07	9.80	72.10	17.02
CTi50Pt3-10	71.5	68	72.6	32	1.51	14.27	62.38	21.83
CTi80Pt3-10	71.3	66	72.3	34	3.60	16.89	56.05	23.47
TiPt3-9	71.4	73	72.3	27	1.95	30.02	0.00	68.03



Fig. 7. Survey and deconvolution of the XPS Ti_{2p} (left) and O₁₅ (right) spectral regions. Line: BE of Ti³⁺ or oxygen linked to Ti³⁺, dashed line for composites.

at binding energy BE = 459.2 eV, 457.9 eV and 456.5 eV are used for the deconvolution of the Ti_{2p} spectral region of catalyst prepared, using pure TiO₂ support (TiPt3) which according to the bibliography [26] correspond to Ti^{4+} , Ti^{3+} and Ti^{2+} species, respectively (Fig. 7). However, only two peaks were needed to fit this Ti_{2p} spectral region for catalysts supported on composites samples. The first one, at 459.3 eV corresponds to Ti^{4+} as previously described, but the band at 458.6 eV, which should be assigned to Ti^{3+} , appears therefore at higher BE (at around 0.7 eV) than on pure titania.

These results point out that Ti-species distribution is quite different in the composites (Ti²⁺ is not detected) and that these species are located in a significantly different environment (with different BE). Moreover, while in the case of TiPt3-9 catalyst 70% of Ti atoms remain unreduced (as Ti⁴⁺) after treatments, this percentage decreases until only 30% for CTi10Pt3-7 catalyst. This fact can be related to the low Ti-content of this support and the reducing character of the carbon matrix, which favours the extent of the Ti-reduction during the pretreatment. The percentage of reduced Ti⁴⁺ quickly increases on higher TiO₂ content in the composite (60% for CTi50Pt3-10 and 66% for CTi80Pt3-10).

Four components were used to fit the O_{1s} spectral region for all samples. In the case of TiPt3-9 the component at 530.7 eV corresponds to the 'bulk' oxygen atom in the stoichiometric TiO₂, and the peaks at 529.3 and 527.9 eV were assigned to oxygen linked to reduced species (Ti³⁺ and Ti²⁺, respectively) [27]. The high BE component, at 532.2 eV, could correspond to various oxygen-

containing surface functional groups. Mainly hydroxyl (–OH) groups were described [28]. When using composite materials as supports, the oxygen distribution species is also influenced by the oxygen content linked to the carbon phase, clearly differentiated because they appeared at higher BE. The peaks at 532.4 and 533.7 eV are assigned to C=O and C=O of carbon phase, respectively [29]. These peaks are predominant in the composites with low TiO₂ content but with increasing this parameter, the main components are located at 530.2 and 531.6 eV associated in this case with oxygen bonded to Ti³⁺ and Ti⁴⁺ species, respectively (Fig. 7). Fig. 7 shows how the BE values of Ti³⁺ and oxygen linked to Ti³⁺ in the composites are around 0.7–1.0 eV higher than those detected for pure titania, which can be due to the ability of the carbon phase to accommodate electrons from the inorganic phase leading to a poorest electronic environment.

The XPS analyses also show the surface concentration and the chemical state of Pt-species (Table 5). A mixture of Pt⁰ and Pt²⁺ with about 70% Pt⁰, was detected in all samples, denoting an insufficient pretreatment or the partial reoxidation of the samples during storage. Regarding the surface Pt concentration (Pt_{XPS}, wt.%), a smooth decrease in the Pt concentration with the increase of TiO₂ loading in the composite, is observed. Usually, this parameter depends on the Pt-particle size (dispersion) and Pt-distribution inside the pores, both effects causing a decrease in the amount of surface Pt detected by XPS. Therefore, the Pt-content decrease could be related to a bigger particle size, but both XRD and HRTEM prove the contrary behaviour. Therefore, this fact could be due to the presence of Pt-particles inside the mesopores. Nevertheless, in spite of that the mesoporosity range should be easily reached by H₂ during chemisorption experiments, the H₂-chemisorption

is quite low according to the Pt-content detected. Therefore, the most plausible explanation to justify the Pt_{XPS} decrease is not sintering or localization inside the pores, but results show again that Pt-species move into the TiO₂ structure through the oxygen vacancies, decreasing the H₂-adsorption and Pt_{XPS} % in spite of the fact that small Pt-particles are actually formed on the surface.

3.2. Catalytic performance

Fig. 8a and b (in order or clarity) shows the evolution of the conversion values obtained with the different catalysts as a function of the reaction time. Clearly, a slower and less active catalyst is obtained depositing the Pt on the pure carbon phase. Although the Pt-activity is favoured on pure TiO₂ regarding the pure carbon phase (reaching total citral conversion after 6 h of reaction), faster hydrogenation processes are always obtained using composites as Pt-supports. With increasing the TiO₂ content of carbon-TiO₂ composites up to CTi40Pt3 catalyst, the reaction rate becomes progressively faster (Fig. 8a). However, catalysts prepared by using composites with a higher TiO₂ content, become progressively slower (Fig. 8b) in such a way that finally composite CTi80 and pure TiO₂ present a similar behaviour (CPt3 < CTi10Pt3 < CTi20Pt3 < CTi30Pt3 < CTi40Pt3 > CTi80Pt3 = CTi80Pt3 = TiPt3).

When comparing the performance of the catalysts in terms of selectivity to unsaturated alcohols (S_{UA}), Fig. 8c and d, the initial S_{UA} values vary in a similar way with the conversion, i.e. they progressively increase from 0% to 40% TiO₂ in the composites and then, progressively decrease, in such a way that CTi80 and pure TiO₂ present again a similar behaviour. These results point out clearly a



Fig. 8. Comparison of the catalytic performance of sample CPt3 (\times), CTi10Pt3 (\bigcirc), CTi20Pt3 (\blacklozenge), CTi30Pt3 (\blacksquare), CTi40Pt3 (\blacklozenge), CTi50Pt3 (\blacklozenge), CTi80Pt3 (+) and TiPt3 (\square). Evolution of conversion with the time of reaction (a, b) and variation of the selectivity to unsaturated alcohols with increasing conversion (c, d). Reaction conditions: citral in heptane solution (0.05 M), 500 mg of catalyst, 1500 rpm, *T* = 90 °C and hydrogen pressure = 8.3 bar.

synergetic effect between both carbon and TiO_2 phases on the Ptactivity and selectivity. Therefore, conversion and selectivity increase with the CTi10 composite regarding pure carbon, but larger carbon contents are necessary in the composite to improve the catalytic performance regarding pure TiO_2 . Clearly, the best catalytic performance is obtained when the TiO_2 proportion in the carbon- TiO_2 supports is around 40% (Fig. 9).

This different catalytic behaviour is obviously a consequence of the different characteristics of the corresponding Pt-active sites. It is well known that the hydrogenation of α - β unsaturated aldehydes is strongly dependent on Pt-dispersion [30-32], i.e. citral hydrogenation is a structure sensitive reaction. In previous works [33] the influence of Pt particle size in the selective hydrogenation of citral has been studied. An increase in the Pt particle size up to around 8 nm produces an increase in both activity and selectivity; however, larger particles cause the contrary effect. On the basis of these results, and considering only the Pt-particle size, a decrease in activity and selectivity increasing the TiO₂ amount should be expected due to the increase in Pt-dispersion in that sense. However, both activity and selectivity increase up to around 40% of TiO₂ in the composite. Consequently, in this catalyst series, dispersion is not the main factor to take into account; the main factor is the synergetic effects between both organic and inorganic phases and the different Pt-support interactions. In fact, the Pt-



Fig. 9. The influence of the support composition on the activity (conversion at 90 min of reaction) and selectivity (at 70% of isoconversion) of supported Pt-catalysts.

concentration in surface determined by XPS analysis (Table 5), is greater for CPt3 and CTi80Pt3 samples, but however, these samples are not the most active or selective catalysts.

The environment of Pt-particles and, consequently, the catalytic performance are related to the TiO₂ content of the support, determining the Pt-support interactions. After thermal treatment in H₂flow, the partial reduction of the TiO₂ phase with formation of oxygen vacancies occurs, which hinders the Pt-sintering but favours the diffusion of Pt-species into the TiO₂ structure. This fact causes an intimate contact between supports and the Pt-active phase, inducing a strong SMSI effect. Therefore, in spite of the loss of accessible Pt-sites, this generates highly active and selective Pt- TiO_2 sites [21]. These sites obviously cannot be formed when using the pure carbon xerogel. Lower conversion values are attached in spite of the catalysts presenting an optimal Pt-particle size (Table 4). Using composites with low amount of TiO_2 (i.e. 10% or 20%), large Pt-agglomerates are still obtained (observed by XRD). which mainly would be localized on the main carbon phase. Nevertheless, both conversion and selectivity increase because the low Ti-content of these samples (the small TiO₂-particle size and the reducing character of the carbon matrix) permits a large reduction of the TiO₂ phase (around 70% of Ti atoms). Increasing the amount of TiO₂ up to 40%, the number of this highly selective and active sites increases, and therefore, the higher are the activity and selectivity. However, at a high TiO_2 content (i.e. 80%), the TiO_2 reducibility decreases due to the larger crystals formed and the rutile formation, decreasing therefore the interaction of C-TiO₂. The Pt-environment depends therefore on the support composition (carbon/TiO₂ ratio), TiO₂ crystal structure and the degree of reduction (formation of vacancies). The electronic δ^+ charge associated with the oxygen vacancies and/or the significant increase in the BE of Pt-species when supported on composites with an intermediate TiO₂ content, can favour the electrophilic adsorption of citral molecules (through the C=O bond), inducing a chemoselective character to the UA formation. Hydrogen is adsorbed and dissociated on the small Pt-nanoparticles of this samples providing a high concentration of atomic hydrogen that therefore favour the C=O hydrogenation to unsaturated alcohols.

This behaviour is also corroborated when analysing the influence of the pretreatment temperature of the CTi20Pt3 sample on the catalytic performance (Fig. 10). As previously commented, the increasing temperature produces a Pt-particle size decrease but the reduction of the TiO₂-phase and the mobility of the Ptspecies are favoured. This fact leads to a significant increase in activity and selectivity.

In this sense it is also interesting to analyse the evolution of the product distribution obtained with the different Pt-catalysts along



Fig. 10. Influence of the pretreatment temperature: 400 °C (_) and 450 °C (_) on the conversion (a) and selectivity (b) of CTi20Pt3 catalyst.



Fig. 11. Evolution of the selectivity values to each product as a function of the conversion reached. Product distributions: Citronellal (\bigcirc), Nerol (\land), Geraniol (\blacktriangle), Citronellol (\bigcirc), 3,7 DMO (\diamond). Reaction conditions: citral in heptane solution (0.05 M), 500 mg of catalyst, 1500 rpm, *T* = 90 °C and hydrogen pressure = 8.3 bar.

the reaction progress, i.e. as the conversion increases (Fig. 11). It is noteworthy that at the beginning of the reaction, geraniol is the main product obtained in all cases except for the CPt3 catalysts. The higher reactivity of geranial, regarding neral in the citral racemic mixture, was previously pointed out [21,33] as a consequence of a smaller steric impediment. It should be noted that when using pure carbon as a Pt-support, CPt3 initially produces citronellal as a main product and confirms that in this case the citral adsorption and hydrogenation is carried out basically through the C=C bonds, while the presence of TiO_2 strongly favours the interaction with the C=O bond. The active sites producing citronellal on the CPt3 catalyst are however quickly deactivated, increasing the selectivity to UA. This behaviour is also observed on the TiPt3 catalysts at short reaction times, where the UA formation is favoured at the expense of the citronellal decrease. At high conversion values however, the formation of citronellol by hydrogenation of the previously formed UA, is favoured due to the low citral concentration.

Using carbon xerogel-TiO₂ composites, the product distribution strongly changes regarding CPt3 even at a low TiO₂ content. In the case of CTi10Pt3, geraniol becomes the main reaction product from the reaction beginning, decreasing the citronellal that is transformed into citronellol along the reaction; however, the hydrogenation of UA seems to be negligible except at high conversion values. Therefore, in the case of the best catalyst prepared, CTi40Pt3, UA (nerol + geraniol) are obtained selectively; only at conversion values higher than 80% UA are hydrogenated to citronellol.

4. Conclusions

Carbon xerogels-TiO₂ composites with different content ratios were successfully prepared. These materials were used as Ptsupports to develop specific hydrogenation catalysts for the conversion of citral into derivative unsaturated alcohols (nerol + geraniol). Reference catalysts using pure phases as supports were also used.

All the textural, chemical, crystallographic and catalytic properties are determined by the TiO_2 content in the composite and by the synergetic effect between both phases. The carbon xerogel is eminently a microporous support, but the composites are mesoporous materials, increasing mesoporosity at the expense of microporosity as increasing the TiO_2 content up to 40 wt.%. The presence of carbon in the composite prevents the TiO_2 crystal growth, and difficults the anatase to rutile transition. Only composites with a TiO_2 content of 80 wt.% present a significant rutile phase. After impregnation and H₂-pretreatment, the partial reduction in the titania phase and certain pore blockage by the Pt-nanoparticles is observed. These nanoparticles are smaller when increasing TiO_2 content, and complementary analysis techniques are necessary in order to obtain a correct interpretation of the results.

Both H_2 -chemisorption and Pt-content are determined by XPS decrease (suggesting sintering) but the XRD peaks corresponding to the Pt-phase decrease and even disappear by increasing the TiO₂ content or treatment temperature. The fact that Pt-dispersion is favoured in this sense was also confirmed by HRTEM. Therefore, the formation of vacancies during pretreatment favours

the mobility of Pt-species inside the TiO_2 -structure, avoiding sintering and improving the metal-support interactions, as demonstrated according to the BE shifting of the XPS spectra.

The combination of oxygen vacancies-Pt was suggested as active and selective sites for the citral hydrogenation. The product distribution significantly changes with the support composition. The adsorption and hydrogenation of citral through the C=C bonds, forming citronellal, are favoured in the beginning of the reaction when using pure carbon as support. However, using composite supports, UA were always the main products. The catalysts developed using a carbon composite containing around 40 wt.% of TiO₂, permit the specific hydrogenation of C=O bonds transforming citral into UA.

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