

Pt–Sn catalysts supported on highly-dispersed ceria on carbon

Application to citral hydrogenation

J.C. Serrano-Ruiz^a, A. Sepúlveda-Escribano^{a,*}, F. Rodríguez-Reinoso^a, D. Duprez^b

^a *Departamento de Química Inorgánica, Universidad de Alicante, Apartado 99, E-03080 Alicante, Spain*

^b *Laboratoire de Catalyse en Chimie Organique (LACCO), UMR 6503, 40 Avenue du Recteur Pineau, 86022 Poitiers Cedex, France*

Received 23 October 2006; received in revised form 11 December 2006; accepted 18 December 2006

Available online 23 December 2006

Abstract

A novel kind of bimetallic Pt–Sn catalysts supported on carbon and promoted with highly-dispersed ceria were prepared by a co-impregnation method and tested in the liquid phase hydrogenation of citral after reduction at low (473 K) and high (773 K) temperatures. They were characterized by N₂ adsorption at 77 K, X-ray diffraction, temperature-programmed reduction (TPR), transmission electron microscopy (TEM) and CO chemisorption at room temperature. Results from N₂ adsorption, XRD and TEM indicated that impregnation method used here led to a highly-dispersed ceria on carbon. Conversely to massive CeO₂, TPR profile of CeO₂/C showed two broad overlapped peaks at low temperatures (803 and 903 K), which are indicative of the easier reduction of the supported promoter. Addition of platinum partially promotes the reduction of surface ceria, this indicating a close metal–promoter interaction. Ceria reducibility was increased with tin addition. The reduction treatment at 773 K produced a strong decrease in the CO adsorption capacity in all cases, although this loss was more relevant for the monometallic catalyst. After reduction at low temperature (473 K), the monometallic Pt/CeO₂/C was the most active catalyst, while the presence of tin reduced the catalytic activity. Reduction at high temperature (773 K) produced the decrease of activity in the case of monometallic sample while bimetallic catalysts, specially the one with Sn/Pt = 0.25, increased the citral conversion values. Reduction treatment at 773 K also increased selectivity to unsaturated alcohols (geraniol and nerol) of bimetallic samples, which presented in all cases higher values than their monometallic counterpart. The onset of new Pt–CeO_x and Pt–SnO_x sites after the reduction process is proposed to explain the increase in activity and selectivity of bimetallic catalysts. © 2006 Elsevier B.V. All rights reserved.

Keywords: Ceria; Carbon; Citral hydrogenation; SMSI; Platinum; Tin

1. Introduction

Noble metal catalysts supported on partially reducible oxides such as CeO₂ present, under certain conditions, the strong metal–support interaction effect (SMSI) [1]. This effect is mainly characterized by a deep change in chemical properties of the dispersed metal phase. Thus, strong inhibition in chemisorptive properties and significant changes in catalytic behaviour occur after reduction treatments at high temperatures [2]. One of the most important probe reactions used to study the existence of SMSI effect in ceria-supported and ceria-promoted noble metal catalysts is the selective hydrogenation of α,β unsaturated aldehydes [3–6]. In this kind of reactions, both the activity and selectivity are generally strongly depen-

dent on the reduction temperature at which catalyst is submitted [7]. The origin of this effect of the activation temperature on the catalytic properties of the metal active phase has been related to its interaction with particles of partially reduced oxide placed at the metal–support interface. These interactions involve the creation of new sites able to selectively interact with the oxygen atom in the carbonyl group, thereby activating the C=O bond. In this way, the most relevant catalytic result of these interactions is an increase of the selectivity to the corresponding unsaturated alcohols.

However, the use of reducible supports is not the only effective strategy to enhance the selectivity to the unsaturated alcohol in noble metal supported catalysts. Thus, the addition of a second more electropositive metal to the catalysts formulation leads to similar effects [8–11]. In this case, the promotion relies on the formation and stabilization of ionic forms of the second metal situated at close vicinity of the active metal particles. These ionic species also would lead to the activation of the C=O bond, in a

* Corresponding author. Tel.: +34 965 90 39 74; fax: +34 965 90 34 54.
E-mail address: asepul@ua.es (A. Sepúlveda-Escribano).

similar way to that of the metal/interface active sites describing the promotion effect of the reducible oxide support.

There is a relatively high number of studies in the literature dealing with the separate promotional effect of a partially reducible oxide support and a second metal in the selective hydrogenation of unsaturated aldehydes. However, the combined effect of both materials on the catalytic properties of the noble metals has received a very scarce attention [7,12,13]. In this work, we pretend to further investigate the combined effect of two promoters (cerium oxide and tin) on the catalytic properties of platinum in the selective hydrogenation of unsaturated aldehydes. To fulfil this goal, a novel kind of Pt–Sn bimetallic catalysts supported on carbon and promoted with highly-dispersed ceria on was prepared. These catalysts were tested in the liquid phase hydrogenation of citral after reduction at low (473 K) and high (773 K) temperature in order to evaluate how the metal–support interactions affect the catalytic performance (activity and selectivity). The catalytic results will be related with characterization data (N_2 adsorption at 77 K, XRD, TEM, TPR, and CO chemisorption at room temperature) in order to obtain information relative to the nature of active sites involved in the catalytic process.

2. Experimental

The CeO_2/C support was prepared by impregnation of the previously out-gassed carbon (Norit, B.E.T. = $790\text{ m}^2\text{ g}^{-1}$) with an acetic solution of $Ce(NO_3)_3 \cdot 6H_2O$ (10 ml of solution per gram of support) with the adequate concentration to obtain a CeO_2 loading of 20 wt%. The excess of solvent was removed by application of vacuum at room temperature. Then, the sample was dried overnight under vacuum at 333 K and calcined in air at 473 K. Pt–Sn/ CeO_2/C catalysts were prepared by co-impregnation with acetic solutions of H_2PtCl_6 (Johnson–Mathey) and $SnCl_2$ (Aldrich, 98%). The excess of solvent was again removed by application of vacuum at room temperature. The Sn/Pt atomic ratio was varied from 0 to 0.75, and the platinum content was 2 wt% in all samples. Thus, the catalysts were labelled as Pt/ CeO_2/C , Pt–Sn (0.25)/ CeO_2/C , Pt–Sn (0.5)/ CeO_2/C and Pt–Sn (0.75)/ CeO_2/C , the number in parentheses indicating the Sn/Pt atomic ratio. No calcination treatment was applied to the catalysts before the reduction step.

The textural properties of the prepared materials were determined by nitrogen adsorption at 77 K with a Coulter Omnisorp 610 system. Before measurements, the samples were dried at 383 K for 12 h and out-gassed at 523 K under vacuum. The micropore volume, V_{micro} , was obtained by application of the Dubinin–Radushkevich (DR) equation to the adsorption isotherm. The volume of mesopores, V_{meso} , was estimated by subtracting the micropore volume from the uptake at a relative pressure of 0.95. The surface area was calculated by application of the B.E.T. method.

X-ray powder diffraction patterns were recorded on a JSO Debye-flex 2002 system, from Seifert, fitted with a Cu cathode an a Ni filter, using a 2° min^{-1} scanning rate.

Temperature-programmed reduction measurements were carried out in a U-shaped quartz cell using a 5% H_2/He gas

flow of $25\text{ cm}^3\text{ min}^{-1}$ and about 0.15 g of sample, with a heating rate of 10 K min^{-1} . Hydrogen consumption was followed by on-line mass spectrometry.

Transmission electron microscopy (TEM) images were obtained with a Philips CM 120 microscope, equipped with an energy-dispersive X-ray detector. The samples were prepared in an ultra-microtome Reichert Ultracut.

CO chemisorption experiments were measured in a static volumetric apparatus described in detail elsewhere [14].

The liquid phase hydrogenation of citral was carried out in a 300 ml stirred autoclave (Autoclave Engineers, fitted with a system for liquid sampling) at 343 K and at constant pressure of 7 MPa. Pre-reduced catalysts (500 mg) were immersed into 90 ml of solvent (isopropanol 99%) without exposure to air before introduction into the autoclave. After a first flush with nitrogen and a second with hydrogen, the temperature was raised to 343 K under 3 MPa of hydrogen. Then a mixture of substrate (3 ml of citral) and of solvent (10 ml) was loaded into the autoclave through a cylinder under a 7 MPa hydrogen pressure. Zero time was taken at this moment and stirring was switched on. Liquid samples were analysed by gas chromatography on a Varian 3400 chromatograph provided with a FID detector and a capillary column DB-WAX (J&W, 30 m, 0.53 mm i.d.) using nitrogen as carrier gas.

3. Results and discussion

3.1. N_2 adsorption isotherms

Fig. 1 shows the N_2 adsorption isotherms at 77 K for supports (parent carbon and CeO_2/C), as well as for the Pt–Sn/ CeO_2/C catalysts. In all cases, type IV isotherms are obtained, in which adsorption and desorption branches are not coincident. This is indicative of the presence of a certain volume of mesopores [15] (see Table 1). A part of the micropores of carbon were blocked after the impregnation with cerium nitrate (V_{micro} decreases from 0.29 to $0.20\text{ cm}^3\text{ g}^{-1}$), and this is accompanied by a decrease in B.E.T. surface area (from 790 to $552\text{ m}^2\text{ g}^{-1}$). This could indicate that the impregnation method used here permits the cerium

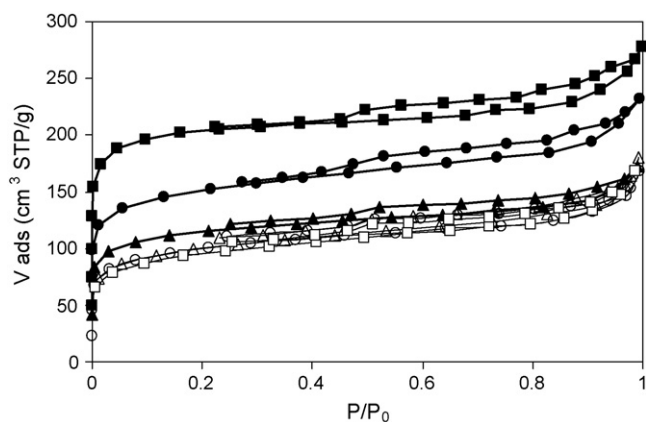


Fig. 1. N_2 adsorption isotherms at 77 K for: (■) carbon; (●) CeO_2/C ; (▲) Pt/ CeO_2/C ; (□) Pt–Sn (0.25)/ CeO_2/C ; (○) Pt–Sn (0.5)/ CeO_2/C ; (△) Pt–Sn (0.75)/ CeO_2/C .

Table 1
Textural properties of the supports and catalysts prepared

	V_{micro} ($\text{cm}^3 \text{g}^{-1}$)	V_{meso} ($\text{cm}^3 \text{g}^{-1}$)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)
Carbon	0.29	0.14	790
CeO ₂ /C	0.20	0.16	552
Pt/CeO ₂ /C	0.17	0.10	428
Pt–Sn (0.25)/CeO ₂ /C	0.15	0.13	366
Pt–Sn (0.5)/CeO ₂ /C	0.14	0.12	363
Pt–Sn (0.75)/CeO ₂ /C	0.14	0.12	348

precursor to access a great part of the carbon porosity. When platinum is added, a slight decrease in surface area was observed (from 552 to 428 $\text{m}^2 \text{g}^{-1}$). In the case of bimetallic catalysts, they showed very similar porosity properties and surface area after the impregnation step.

3.2. XRD patterns

Fig. 2 shows the X-ray diffraction patterns obtained for the CeO₂/C support (after treatment in air at 473 K) as well as for the Pt–Sn/CeO₂/C catalysts. Four peaks (dashed lines) at 2θ values of 28.6, 33.4, 47.8 and 56.7 were detected in all cases. These peaks are produced, respectively, by the reflections of the (1 1 1), (2 0 0), (2 2 0) and (3 3 1) crystallographic planes of the cubic CeO₂ phase [16]. The presence of broad diffraction peaks in all cases is indicative of small CeO₂ crystals (5.4 nm, estimated from the (1 1 1) diffraction line broadening) and thus, a high dispersion of the cerium oxide phase on the carbon support. This value for the ceria crystal size is in good agreement with those obtained by Silvestre-Albero et al. in Pt/CeO₂–SiO₂ catalysts (5.8 nm) [4]. No peaks corresponding to platinum or tin species were detected in the XRD patterns.

3.3. Temperature-programmed reduction (TPR)

Fig. 3 shows the temperature-programmed reduction profiles (H₂ consumption) obtained with the CeO₂/C support and the Pt–Sn/CeO₂/C catalysts. The TPR profile of CeO₂/C exhibited two broad overlapped peaks centred at around 803 and

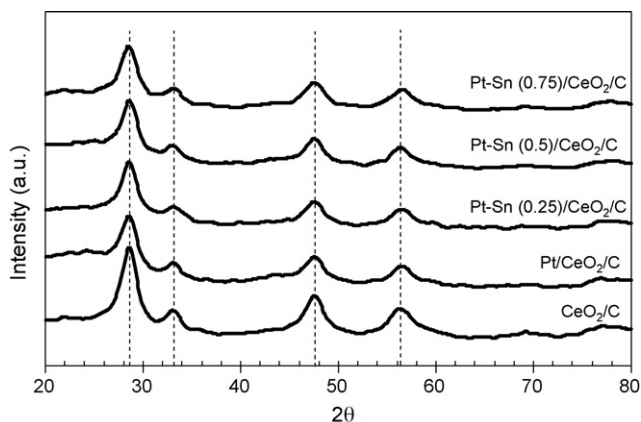


Fig. 2. XRD patterns for CeO₂/C support and Pt–Sn/CeO₂/C catalysts.

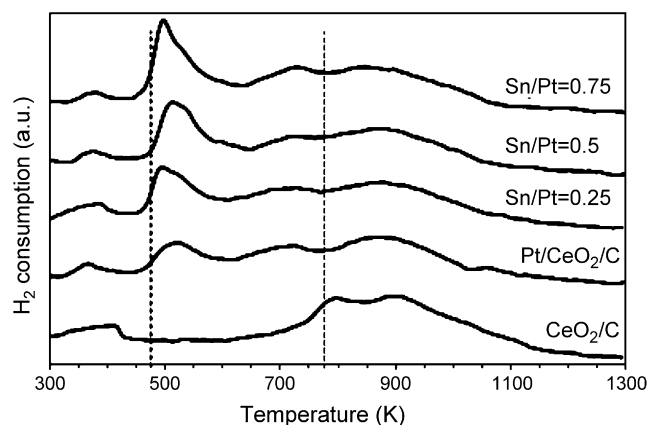


Fig. 3. TPR profiles of the CeO₂/C support and Pt–Sn/CeO₂/C catalysts.

903 K, respectively. The typical TPR profile for unsupported CeO₂ includes two reduction peaks, a small one at low temperature (773–823 K) and the second one, much more prominent, at higher temperatures (1163–1173 K), which are respectively associated to the reduction of surface and bulk ceria [3,17,18]. Furthermore, it has been observed that the size of the reduction peak at low temperature increases with the surface area of CeO₂ [19,20]. In the present case, only a continuous reduction process was observed at low temperatures (773–873 K). This could be indicative, as already pointed out, of a high dispersion of cerium oxide on the carbon support, with a very small CeO₂ particle size; this would lead to an easier reduction of ceria phase with respect to the unsupported oxide.

In the case of Pt/CeO₂/C, the reduction profile showed the onset of one new reduction peak at lower temperature (531 K), while the two big overlapped peaks are shifted to lower temperatures (726 and 878 K). This indicates that the presence of platinum partially promotes the reduction of ceria via spill over of hydrogen from platinum particles to the support [3,21]. Thus, the peak at lower temperature can be assigned to the surface reduction of CeO₂ in close contact with platinum, this accounting for a strong interaction between the metallic phase and cerium oxide in this catalyst. The reduction profiles for the bimetallic Pt–Sn/CeO₂/C catalysts showed the same feature than the monometallic Pt/CeO₂/C, with a peak at low temperature (503–513 K) and two broad overlapped reduction peaks at around 723 and 873 K. It is interesting to observe that the size of the peak at low temperature was higher for bimetallic catalyst than for the monometallic counterpart. Furthermore, the area of this low temperature peak increased with the tin content. This could be indicative of reduction of ionic tin species, although the tin loading in catalysts is too low to produce such increase only by itself. This reduction peak, as in the case of the monometallic sample, can be also due to the surface reduction of cerium oxide in close contact with platinum. Thus, it seems that the presence of tin facilitates the transport of hydrogen via spill over from the platinum surface to the ceria particles in close contact with metal. This fact indicates that the reducibility of ceria is improved in the case of bimetallic catalysts, as previously reported [4,14,22].

It should be noted that, as indicated with dashed lines in Fig. 3, reduction treatment at 473 K should not produce appreciable ceria reduction in the catalysts under study. However, the treatment at high temperature (773 K) is enough to produce the surface reduction of ceria and only the bulk part of the oxide, represented by the second of the overlapped peaks, remain unreduced after this treatment. This fact implies the creation of oxygen vacancies (CeO_x) and the presence of Ce^{3+} ions located principally in the vicinity of platinum particles. With regard to tin, the reduction profiles of bimetallic catalysts did not permit to establish a specific zone where tin is reduced. It seems clear that tin enhances the surface ceria reduction process but, at the same time, it has been previously observed that the presence of cerium retards the reduction of tin, which remains mainly as ionic tin after a reduction treatment at 773 K [14,22].

3.4. Transmission electron microscopy (TEM)

Fig. 4 shows the TEM images for the Pt/CeO₂/C catalyst, as a representative sample. Dark zones are due to cerium oxide, while light parts indicate the presence of carbon. From the low magnification pictures (Fig. 4a and b) it can be seen that cerium oxide is well spread on the carbon surface. It is also well appreciated in Fig. 4b that a thin film of CeO₂ entirely covers the carbon particle, reaching almost all its porosity. This would indicate, as we have pointed above, that the preparation method used here leads to a highly-dispersed CeO₂ phase on carbon support. In order to evaluate the degree of dispersion of ceria on the carbon support a set of high magnification images (including the ones represented in Fig. 4c and d) were analyzed for the representative sample Pt/CeO₂/C in fresh and reduced at 773 K states.

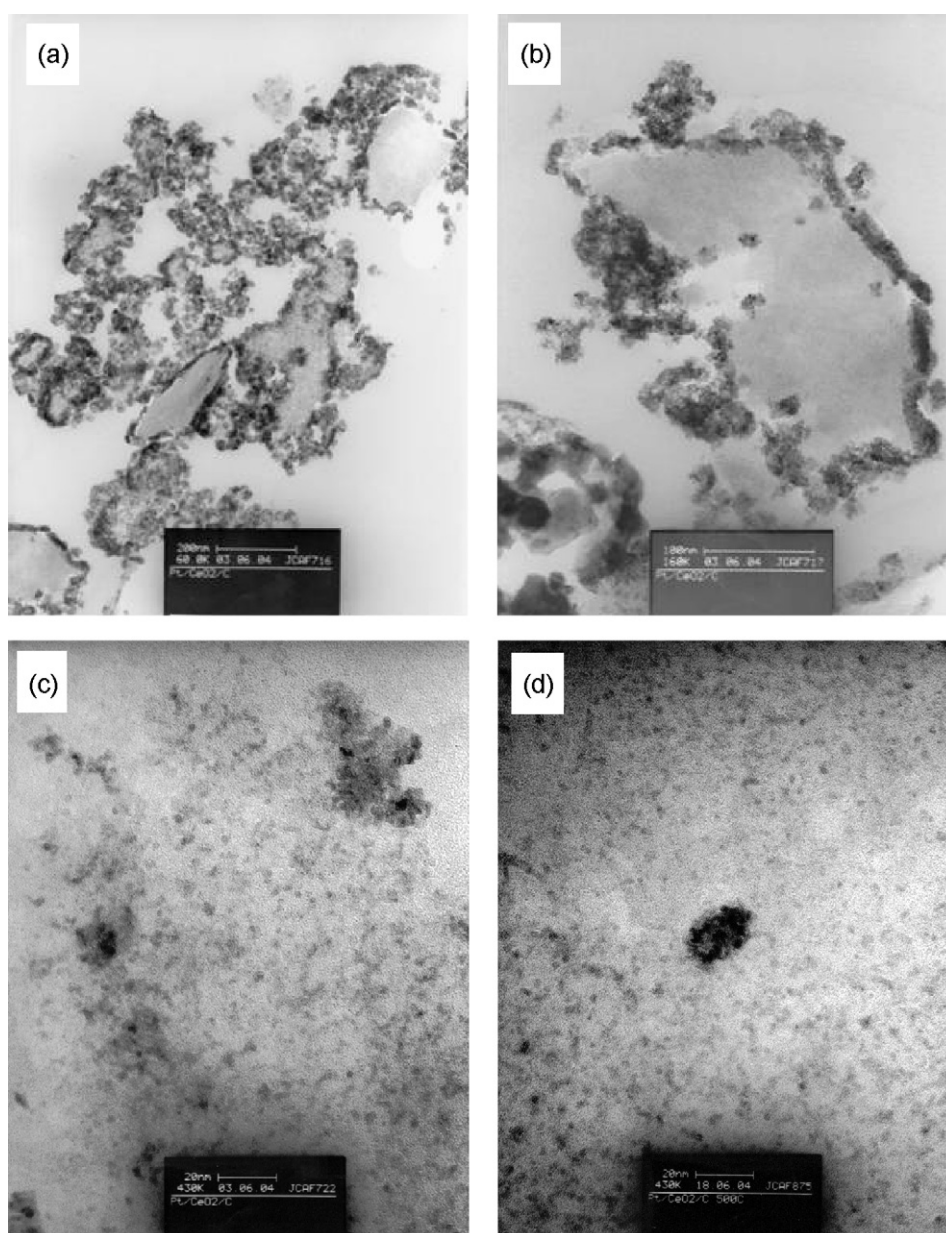


Fig. 4. TEM micrographs at different magnification (a)–(c) of fresh, and (d) reduced at 773 K Pt/CeO₂/C catalyst.

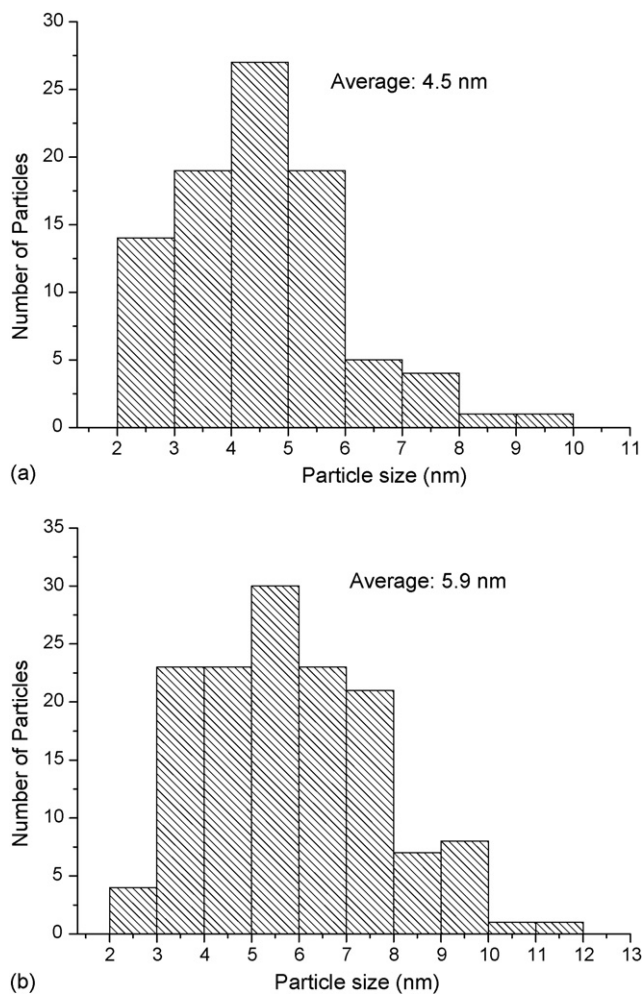


Fig. 5. CeO₂ particle size distribution histograms for Pt/CeO₂/C obtained by TEM: (a) fresh and (b) reduced at 773 K.

Thus, a great number of ceria particles were measured and the results of these analyses are exposed in Fig. 5. It can be seen that the particle size distribution for the fresh sample (Fig. 5a) is centred around 4–5 nm (average size 4.5 nm), in good agreement with the mean ceria crystal size estimated from the (1 1 1) XRD line broadening (5.4 nm) showed in a previous section. After the reduction treatment at high temperature (773 K), a broader particle size distribution was obtained (Fig. 5b), with a higher average size (5.9 nm) and the main part of ceria particles being larger than 5 nm. This is a clear evidence of a sintering of the partially reduced ceria phase upon the thermal reduction treatment, which has been previously reported for carbon supported CeO₂–Pt catalysts [23]. Since the dark CeO₂ phase almost totally surrounds the carbon particles, it was not possible to distinguish the presence of platinum and/or tin in any case. Thus, in order to evaluate the platinum dispersion on the catalysts surface, alternative measurements such as CO chemisorption at room temperature were used.

3.5. CO chemisorption at room temperature

Fig. 6 shows the CO chemisorption isotherms at room temperature for the catalysts under study, reduced at both 473 and 773 K. It can be seen that reduction treatment at high temperature produced a decrease in the CO adsorption capacity in all cases. However, this drop is more relevant for the monometallic sample. A strong interaction of the platinum crystallites with particles of partially reduced ceria (CeO_x) placed at the metal–support interface can account for the observed decrease in the CO uptake. This interaction could involve electronic (from the reduced ceria particles to platinum aggregates) and geometric (covering of platinum particles by patches of reduced ceria) effects, although the latter has been probed to

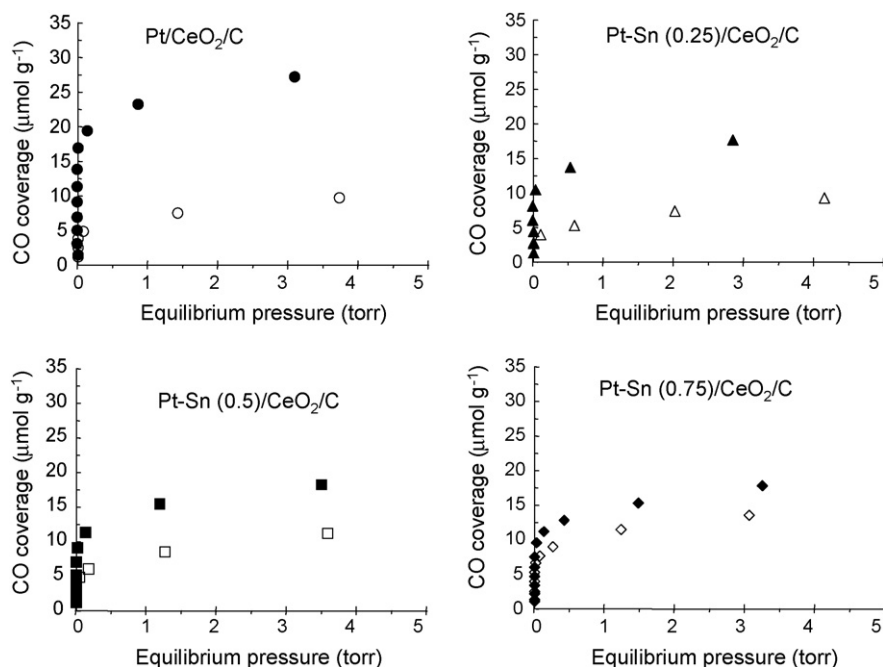


Fig. 6. CO chemisorption isotherms at 298 K for Pt–Sn/CeO₂/C catalysts after reduction at 473 K (full symbols) and 773 K (open symbols).

need higher reduction temperatures than the used in the present work (973 K) [1]. Furthermore, taking into account the results of the previous section, a certain contribution of encapsulation of platinum particles associated with ceria sintering cannot be ruled out.

In the case of bimetallic samples, the treatment at low temperature (473 K) already produces a decrease in CO uptakes with regard to monometallic catalyst. This could be due to a covering of platinum particles by ionic tin species. Thus, the co-impregnation method used here would permit a close interaction between both metals even after such a low reduction temperature. After reduction at high temperature, besides ceria, tin also can contribute to the blocking of platinum sites accounting for the loss of CO adsorption capacity in bimetallic samples.

It is necessary to have in mind that a parallel adsorption of CO on ceria could also take place. However, it is well known that the use of chlorinated metal precursors strongly decreases the magnitude and the rate of CO adsorption on ceria. Furthermore,

the very low CO pressures at which the adsorption isotherms have been measured may limit the extent of parallel CO adsorption by the support. Thus, the weight of this parallel adsorption of CO on ceria in the global adsorption process would not be relevant.

3.6. Catalytic behaviour

Fig. 7 shows the main reactions pathways that can occur during citral hydrogenation. The hydrogenation of the carbonyl group gives the corresponding unsaturated alcohols (nerol and geraniol), whereas the hydrogenation of the conjugated C=C bond gives citronellal. Consecutive hydrogenation leads to citronellol and finally to the saturated alcohol 3,7-dimethyloctanol. At the same time, citronellal can produce secondary products by processes of cyclization (*iso*-pulegol) or reaction with the solvent (acetals of citronellal). These side reactions have been probed to take place in acid sites situated on the support [7] and thus, their formation strongly depends on the nature and

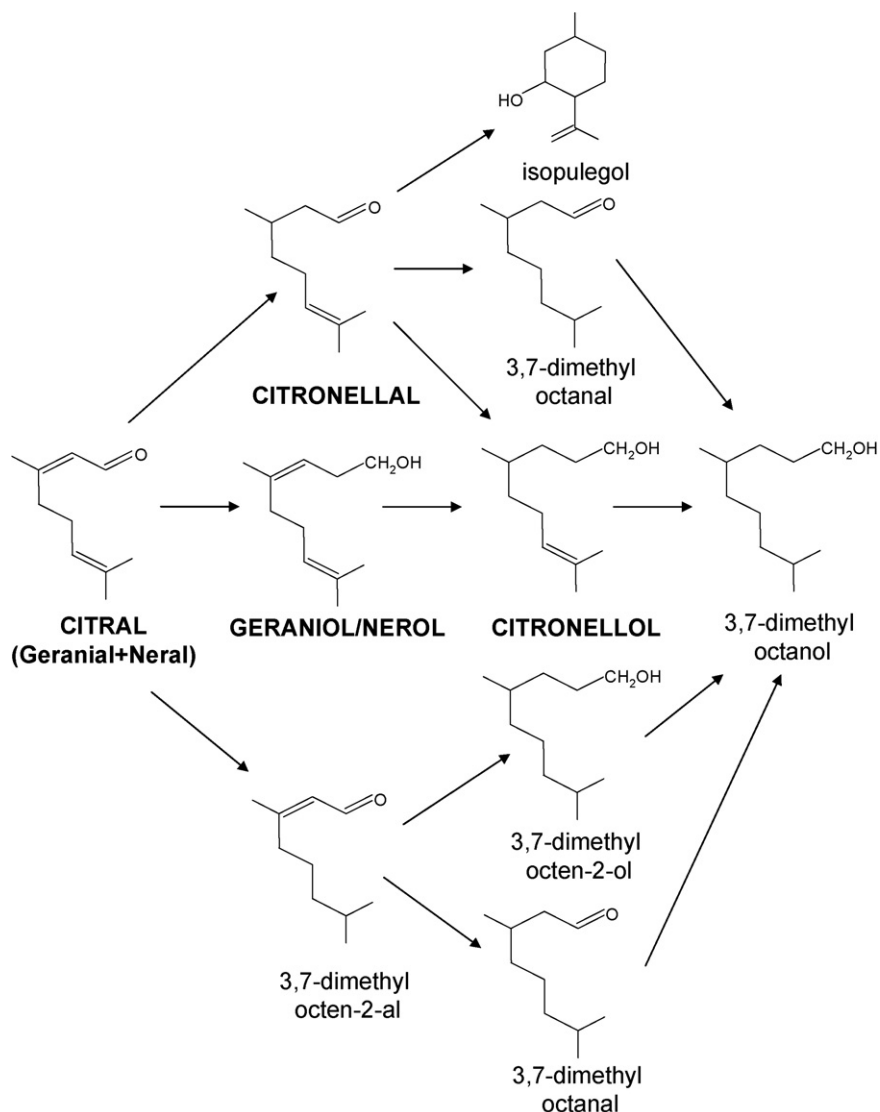


Fig. 7. Reaction scheme for citral hydrogenation.

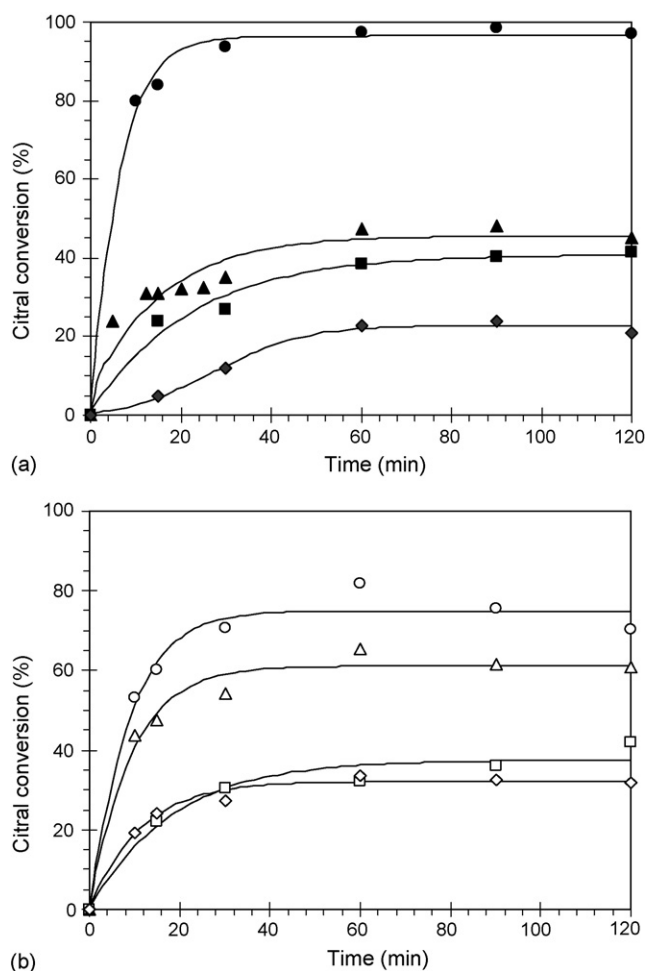


Fig. 8. Citral conversion as function of reaction time for (●) Pt/CeO₂/C; (▲) Pt-Sn 0.25; (■) Pt-Sn 0.5; (◆) Pt-Sn 0.75 after reduction at (a) 473 K and (b) 773 K.

even of the surface area of the material [24]. Under the experimental conditions used in the present work, the main products observed were citronellal, the unsaturated alcohols (geraniol and nerol) and the saturated alcohol citronellol. The production of side products was low in our catalysts, this fact being previously related to the presence of cerium [25].

Fig. 8a shows the citral conversion as function of time for the catalysts previously reduced at 473 K. It can be observed that a rapid hydrogenation of citral occurs during the first 30 min and, after this earlier period, the citral conversion reaches a stable value in all cases. This deactivation observed could be related to processes of citral decomposition or of poisoning of active sites responsible for hydrogenation by CO and carbonaceous species yielding from reactions of the formed unsaturated alcohols [26–29]. Pt/CeO₂/C was the most active catalyst after reduction at 473 K, reaching a citral conversion value close to 100% after 30 min of reaction. With regard to bimetallic catalysts, they showed lower conversion values than the monometallic sample in all the range of reaction times. Furthermore, the higher tin content in catalysts the lower citral conversion values were found. Since at such low reduction temperature no SMSI effect was expected to occur, this could be due to a lower number of

accessible platinum active sites for citral hydrogenation after tin addition, in good agreement with the results exposed in the previous section.

When the catalysts were reduced at 773 K (Fig. 8b) a similar conversion–reaction time profile was observed in all cases. The conversion followed the order: Pt/CeO₂/C > Pt-Sn(0.25)/CeO₂/C > Pt-Sn(0.5)/CeO₂/C ≈ Pt-Sn(0.75)/CeO₂/C. However, if conversion values after reduction at both low and high temperatures are compared, different behaviours could be observed. On one hand, citral conversion decreased for monometallic Pt/CeO₂/C after reduction at high temperature. The strong interaction of reduced ceria particles with platinum after this treatment would produce the decrease in the number of available sites for hydrogenation (Fig. 6), with the subsequent loss of activity. In the case of bimetallic samples, the decrease in CO saturation coverage (Fig. 6) is not accompanied by a decrease in activity, but it increases with the reduction temperature. This increase is relevant for sample with Sn/Pt=0.25 (from 35 to 54% conversion at 30 min of reaction) and less pronounced for the other two bimetallic catalysts. It seems that the reduction treatment at high temperature favours the creation of new active sites for the hydrogenation of citral accounting for the increase in conversion values.

In order to add light to the nature of these new active sites, the effect of the reduction temperature on the selectivity toward the unsaturated alcohols was also evaluated (Fig. 9). It is remarkable that the reduction treatment at 773 K enhanced the selectivity to unsaturated alcohols in all cases. Furthermore, bimetallic catalysts showed higher selectivities than the monometallic sample. In the case of Pt/CeO₂/C the beneficial effect (in terms of selectivity) observed after reduction at 773 K could be explained by two effects of the CeO₂ promoter: on one hand, the creation of new Pt–CeO_x sites at the metal–support interface acting as acid Lewis sites able to activate the C=O bond of the citral molecule; on the other hand, some authors have proposed the existence of an electronic interaction between the reduced ceria particles and the active metal which leads to an increase in electron density of platinum particles with the subsequent weakening of adsorption of citral via the C=C bond [25,30,31]. With regard to bimetal-

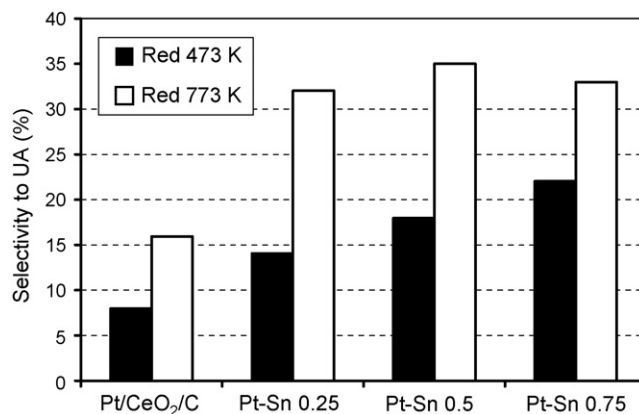


Fig. 9. Selectivity to unsaturated alcohols (geraniol+nerol) for the Pt-Sn/CeO₂/C catalysts after reduction at low (473 K) and high (773 K) temperature.

lic catalysts, the additive presence of Sn^{m+} species, also able to act as Lewis acid sites, on the surface of platinum particles and/or in their close vicinity could account for the increase in selectivity to unsaturated alcohols with reduction temperature. The increase of conversion after reduction at high temperature in these catalysts could be also explained by the creation of new Pt– Sn^{m+} sites active for hydrogenation of the C=O bond in the citral molecule.

4. Conclusions

A novel kind of bimetallic Pt–Sn catalysts supported on carbon and promoted by highly-dispersed ceria were prepared by a co-impregnation method and tested in the liquid phase hydrogenation of citral after reduction at low (473 K) and high temperature (773 K). N_2 adsorption at 77 K indicated that the impregnation method used here allows the cerium precursor to reach the main part of the carbon porosity. XRD and TEM data also supported that cerium dioxide is in a highly-dispersed state on the carbon support. The TPR profile of the CeO_2/C support included two broad low temperature reduction peaks, this indicating a small CeO_2 crystal size. TPR data from Pt/ CeO_2/C indicated that Pt and cerium are in close contact. When tin is added, ceria reducibility was increased. After reduction at low temperature (473 K), the monometallic Pt/ CeO_2/C was the most active catalyst, while the presence of tin reduced catalytic activity, in agreement with the results of CO chemisorption indicating a lower availability of platinum sites. Reduction at high temperature (773 K) produced the decrease of activity in the case of the monometallic sample, while bimetallic catalysts increased their conversion values. Reduction at 773 K increased the selectivity to unsaturated alcohols (geraniol and nerol) in all cases, although bimetallic catalysts showed higher values than the monometallic sample. The presence of new Pt– CeO_x and Pt– SnO_x sites after reduction at high temperature is proposed to explain the increase in activity and selectivity for bimetallic catalysts.

Acknowledgements

Financial support by the Comisión Interministerial de Ciencia y Tecnología (Projects BQU 2000-0467 and BQU 2003-06150), as well as those from Generalidad Valenciana (GRUPOS03-212) and Universidad de Alicante (VIGROB-082) is gratefully acknowledged. J.C. Serrano-Ruiz also thanks Ministerio de Educación y Ciencia (Spain) for its FPI grant.

References

- [1] S. Bernal, J.J. Calvino, M.A. Cauqui, J.M. Gatica, C. Larese, J.A. Pérez-Omil, J.M. Pindado, *Catal. Today* 50 (1999) 175.
- [2] G.L. Haller, D.E. Resasco, *Adv. Catal.* 36 (1989) 173.
- [3] A. Sepúlveda-Escribano, F. Coloma, F. Rodríguez-Reinoso, *J. Catal.* 178 (1998) 649.
- [4] J. Silvestre-Albero, F. Rodríguez-Reinoso, A. Sepúlveda-Escribano, *J. Catal.* 210 (2002) 127.
- [5] M. Abid, G. Ehret, R. Touroude, *Appl. Catal. A: Gen.* 217 (2001) 219.
- [6] M. Abid, V.P. Boncour, R. Touroude, *Appl. Catal. A: Gen.* 297 (2006) 48.
- [7] A. Silva, O. Santos, M. Mendes, E. Jordao, M. Fraga, *Appl. Catal. A: Gen.* 241 (2003) 155.
- [8] G. Lafaye, T. Ekou, C. Micheaud-Especel, C. Montassier, P. Marecot, *Appl. Catal. A: Gen.* 257 (2004) 107.
- [9] I. Vilella, S.R. de Miguel, C. Salinas-Martínez de Lecea, A. Linares-Solano, O.A. Scelza, *Appl. Catal. A: Gen.* 281 (2005) 247.
- [10] S. Recchia, C. Dossi, N. Poli, A. Fusi, L. Sordelli, R. Psaro, *J. Catal.* 184 (1999) 1.
- [11] E. Asedegbega-Nieto, B. Bachiller-Baeza, A. Guerrero-Ruiz, I. Rodríguez-Ramos, *Appl. Catal. A: Gen.* 300 (2006) 120.
- [12] A. Silva, E. Jordao, M. Mendes, P. Fouilloux, *Appl. Catal. A: Gen.* 148 (1997) 253.
- [13] P. Reyes, H. Rojas, J.L.G. Fierro, *J. Mol. Catal. A: Chem.* 203 (2003) 203.
- [14] J.C. Serrano-Ruiz, G.W. Huber, M.A. Sánchez-Castillo, A. James, A. Dumesic, F. Sepúlveda-Escribano, Rodríguez-Reinoso, *J. Catal.* 241 (2006) 378.
- [15] S.J. Gregg, K.S.W. Sing, *Adsorption Surface Area and Porosity*, Academic Press, London, 1967.
- [16] JCPDS file 34-0394. International Centre for Diffraction Data.
- [17] H.C. Yao, Y.F.Y. Yao, *J. Catal.* 86 (1984) 254.
- [18] F. Fally, V. Perrichon, H. Vidal, J. Kaspar, G. Blanco, J.M. Pintado, S. Bernal, G. Colon, M. Daturi, J.C. Lavalley, *Catal. Today* 59 (2000) 373.
- [19] E. Aneggi, M. Boaro, C. de Leitenburg, G. Dolcetti, A. Trovarelli, *J. Alloys Compd.* 408–412 (2006) 1096.
- [20] F. Giordano, A. Trovarelli, C. de Leitenburg, M. Giona, *J. Catal.* 193 (2000) 273.
- [21] C. Bozo, N. Guihaume, E. Garbowski, M. Primet, *Catal. Today* 59 (2000) 33.
- [22] J.C. Serrano-Ruiz, A. Sepúlveda-Escribano, F. Rodríguez-Reinoso, Meeting of the Spanish Society of Catalysis SECAT, Torremolinos, Spain, 2003, p. 51 (abstracts).
- [23] A. Sepúlveda-Escribano, J. Silvestre-Albero, F. Coloma, F. Rodríguez-Reinoso, *Stud. Surf. Sci. Catal.* 130 (2000) 1013.
- [24] C. Milone, C. Gangemi, R. Ingoglia, G. Neri, S. Galvagno, *Appl. Catal. A: Gen.* 184 (1999) 89.
- [25] B. Bachiller-Baeza, I. Rodríguez-Ramos, A. Guerrero-Ruiz, *Appl. Catal. A: Gen.* 205 (2001) 227.
- [26] U.K. Sing, M.A. Vannice, *J. Catal.* 191 (2000) 165.
- [27] U.K. Sing, M.A. Vannice, *J. Catal.* 199 (2001) 73.
- [28] A. Waghay, D.G. Blackmond, *J. Phys. Chem.* 97 (1993) 6002.
- [29] S. Nishiyama, T. Hra, S. Tsuruya, M. Masai, *J. Phys. Chem. B* 103 (1999) 4431.
- [30] P. Claus, *Top. Catal.* 5 (1998) 51.
- [31] P. Gallezot, D. Richard, *Catal. Rev. Sci. Eng.* 40 (1998) 81.