Pt, PtSn and PtGe catalysts supported on granular carbon for fine chemistry hydrogenation reactions

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Abstract

Two series of PtSn and PtGe catalysts with different metallic loadings, supported on activated carbon powder, were prepared by successive impregnation. Both the effects of the second metal addition and the Sn or Ge loading on the activity and selectivity in the carvone and the citral hydrogenations (used as catalytic tests) were investigated. In all cases the support was purified to eliminate undesirable elements such as sulfur and, for high Pt loadings, carbon was functionalized with nitric acid so as to introduce more oxygen-containing groups. The carvone hydrogenation was carried out with PtSn catalysts, the Pt and Sn loadings being very low. The citral hydrogenation was carried out with PtSn and PtGe catalysts with higher metal loadings supported on both purified, and purified and functionalized carbons. Besides, the effect of the branched solvent in the activity and selectivity of the citral hydrogenation reaction was also studied with PtSn catalysts. The catalysts were characterized by temperature-programmed reaction (TPR), test reactions of the metallic phase (cyclohexane dehydrogenation and cyclopentane hydrogenolysis), hydrogen chemisorption and by X-ray photoelectron spectroscopy (XPS).

The catalytic activity in the carvone hydrogenation showed a maximum for the monometallic catalyst with respect to the Sn loading. For the catalyst with the highest tin loading (0.4 wt%) even though the activity drastically decreased, the selectivity to the doubled unsaturated alcohol (carveol) was very important.

Although the citral hydrogenation gave very good results with PtSn systems with high metallic loadings, the opposite happened with the PtGe ones. Moreover, the more branched solvents modified the selectivity to unsaturated alcohols of the PtSn catalyst in the citral hydrogenation.
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1. Introduction

One of the most important current use of carbon as a support is in liquid-phase hydrogenation reactions catalyzed by mono and bimetallic systems [1] and, among them, the hydrogenation of aldehydes and ketones. However, the literature is scarce about mono and bimetallic catalytic systems used for the selective carvone hydrogenation [2–4]. On the other hand, it could be mentioned studies using Pt–Co, Pt–Ru, Pt–Sn, Pt–Ga, etc. for selective hydrogenation of $\alpha - \beta$ unsaturated ketones and aldehydes such as crotonaldehyde, acrolein, cinnamaldehyde, thymol, etc. [5,6]. As it was mentioned, few papers about the use of supported mono and bimetallic systems (such as Pt, Rh and Pt–Au)

for the selective hydrogenation of carvone have been reported in the literature [2–4]. Carvone is a monocyclic terpenic ketone which has three sites to be hydrogenated, viz., a C=O group, an endocyclic C=C group and an exocyclic one. This molecule has a rigid structure, the π electrons of the double C=C bonds are more available to react with electrophilic reagents than the strong σ bonds. The aim is to optimize the production of unsaturated ketones and mainly of the unsaturated alcohols which are the most valuable products [5]. Fig. 1 shows the reaction scheme of the carvone hydrogenation. Carvone is a component of caraway, dill and spearmint seeds. It has a lot of uses as flavor, antibacterial and antifungical agent, repellent of the fruit fly and in the cosmetic industry [7].

The citral (3,7-dimethyl-2,6-octadienal) is a multi-unsaturated compound, and it is one of the main components of the lemongrass oil. It has a carbonyl group, a double C=C bond conjugated with the carbonyl group, and an isolated C=C
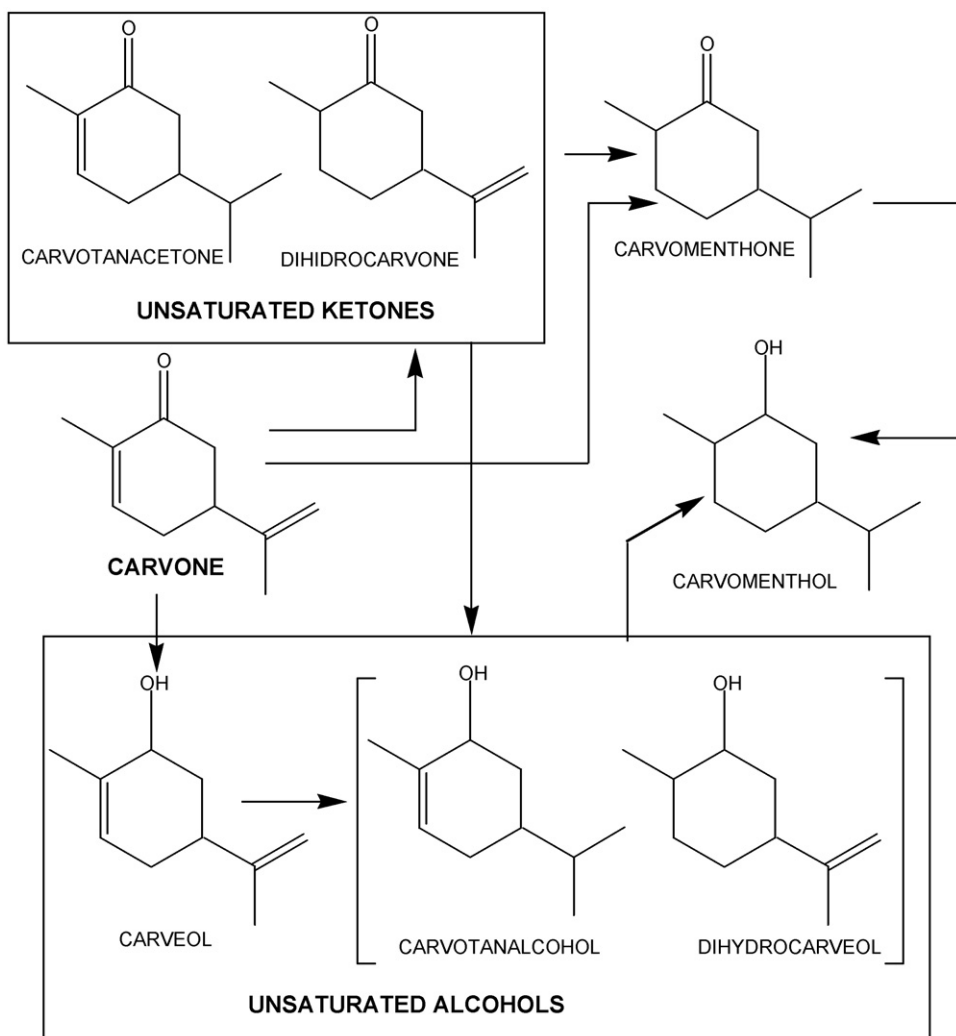
Fig. 1. Reaction scheme of carvone hydrogenation.

double bond. It also exists as *cis* and *trans* isomers and it can also be cyclized. The hydrogenation products have all important uses in the synthesis of flavors and also in pharmaceutical and cosmetic industries [8–10]. The citral hydrogenation is complex since many side reactions such as cyclization and acetalization (produced by a reaction of the solvent with both citral and citronellal, which is catalyzed by acidic sites of the supports) could take place [11]. Fig. 2 shows the reaction scheme of citral hydrogenation.

The aim of this paper is to study the behavior of PtSn and PtGe catalysts supported on activated carbon purified and also functionalized with nitric acid in the hydrogenation of carvone and citral. The correlation of their catalytic behavior with the characteristics of the metallic phase is also analyzed.

2. Experimental

A commercial granular carbon derived from a pit of peach (GA-160 from Carbonac) was crushed and sieved to a final particle size between 100 and 140 mesh, its original impurity content being 2.9 wt% (K: 1.23, Ca: 0.41, Na: 0.46, Mg: 0.07, Si: 0.12,

P: 0.09, Cl: 0.44 and S: 0.03 wt%). The textural properties of the carbon were $S_{BET} = 987 \, m^2 \, g^{-1}$, $V_{micropore} = 0.33 \, cm^3 \, g^{-1}$. This support, called as C, was then purified (elimination of inorganic impurities) by successive treatments with aqueous solutions (10 wt%) of HCl, HNO_3 and HF, respectively, at room temperature for 48 h without stirring. After HCl and HNO_3 treatments, the support was repeatedly washed with de-ionized water up to a final pH 4. After the HF treatment, it was washed with de-ionized water up to the final pH of the water used for washing, and then it was dried at 120 °C. In order to eliminate sulfur compounds, the acid-treated carbons were submitted to a thermal treatment under hydrogen flow (5 ml H_2 min^{-1} g^{-1}) at 850 °C for 8 h. After the purification step and the hydrogen treatment at high temperature, the impurity content of the granular carbon (called C-P) was dramatically reduced, viz., Na: 0.0105, Mg: 0.011, Si: 0.019, P: 0.015, K: 0.03, Ca: 0.047, Fe: 0.038, Cl: 0.016 and S: 0.0105 wt%. It is worth mentioning that the textural properties only slightly changed, the S_{BET} being 976 m^2 g^{-1} and the micropore volume remaining practically constant. One fraction of the purified support was submitted to a functionalization treatment with aqueous solution of HNO_3. This treatment
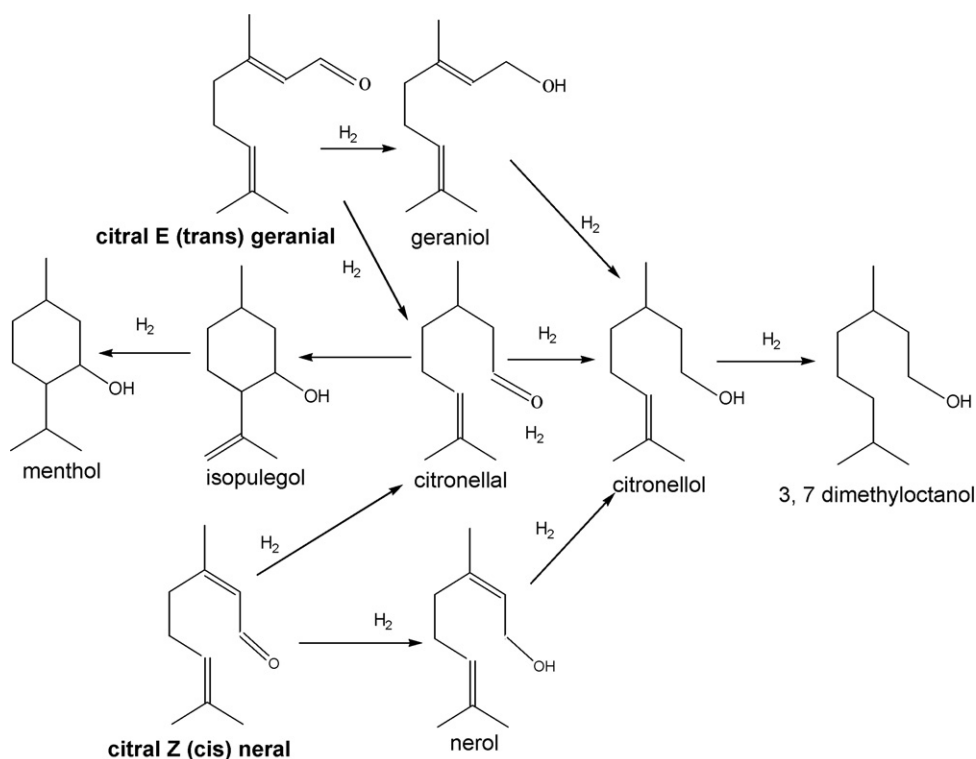
Fig. 2. Reaction scheme of citral hydrogenation.

was carried out at 25 °C for 48 h. The concentration of the solution was 10 wt%. The functionalized support was called "C-PN". After the functionalization treatment, the samples were dried at 120 °C overnight. Again, the functionalization treatment did not modify the carbon textural properties [12].

The monometallic Pt catalysts were prepared by conventional impregnation of the supports (C-P or C-PN) with aqueous solution of H_2PtCl_6. The total amount of Pt in the impregnating solution was such as to obtain the corresponding Pt loading (1 ± 0.05 and 5 ± 0.05 wt%). The catalyst precursors were dried at 120 °C overnight. Bimetallic PtSn catalysts were prepared by impregnation of the monometallic catalyst precursor based on C-P carbon with a hydrochloric solution of $SnCl_2$. The total Sn amount in the impregnating solution was such as to obtain the desired Sn loadings in the bimetallic catalysts. PtGe catalysts based on C-P and C-PN carbons were prepared by successive impregnation using a $GeCl_4$ solution as a Ge precursor. In all cases, impregnations were carried out at 25 °C for 6 h using a volume of impregnation solution/mass of support ratio of 30 ml g^{-1}, and a stirring rate of 600 rpm. All the characteristics of the studied catalysts are shown in Table 1.

The carvone hydrogenation was carried out in discontinuous equipment with a device for sampling the reaction products. The reaction was carried out at 40 °C and atmospheric pressure. Toluene (pure, from Merck) was used as a solvent. The volume of solvent, the carvone amount (98%, Aldrich) and the catalyst weight used in the experiments were 20 ml, 0.09 g, and 0.050 g, respectively. Prior to the reaction, catalysts were reduced "in situ" at 350 °C under flowing H_2 for 3 h.

The citral hydrogenation was carried out in the same equipment that was used for the carvone hydrogenation. The reaction was performed at 70 °C and atmospheric pressure. Pure 2-propanol was used as solvent. In order to study the solvent effect, 2-pentanol and *tert*-butanol were also used with a PtSn/C-P catalyst. The volume of solvent, the citral amount (Sigma, 61% *cis*- and 36% *trans*-) and the weight of catalyst used in the experiments were 30 ml, 0.30 ml, and 0.30 g, respectively. Prior to the reaction, catalysts were reduced "in situ" under flowing H_2 at 350 °C for 3 h. In both hydrogenation processes, the reaction mixture was stirred at 1400 rpm and the products were analyzed

Table 1
Characteristics of the studied catalysts

Catalysts	Designation	%Pt	Sn(wt%) or Ge(wt%)	(Sn/Pt) or (Ge/Pt) atomic
Pt/C-P	A	1	–	–
PtSn/C-P	ASn013	1	0.13	0.21
PtSn/C-P	ASn04	1	0.4	0.66
Pt/C-P	B	5	–	–
PtSn/C-P	BSn1	5	1	0.33
PtSn/C-P	BSn2	5	2	0.66
PtSn/C-P	BSn3	5	3	0.98
PtGe/C-P	BGe1	5	0.61	0.33
PtGe/C-P	BGe2	5	1.83	0.98
Pt/C-PN	C	5	0.61	–
PtGe/C-PN	CGe1	5	0.08	0.04
PtGe/C-PN	CGe2	5	0.22	0.12
PtGe/C-PN	CGe3	5	0.61	0.33
PtGe/C-PN	CGe4	5	1.83	0.98

in a GC chromatographic system by using a Supelcowax 10 M column and a FID as detector. The detected products were the ones seen on Figs. 1 and 2. From previous experiments, diffusional limitations were found to be absent under these conditions [13].

Catalysts were characterized by test reactions of the metallic phase (cyclohexane dehydrogenation, CHD, and cyclopentane hydrogenolysis, CPH), temperature-programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS) and hydrogen chemisorption measurements.

Test reactions were carried out in a flow reactor. CHD was carried out at 320 °C by using a H_2/CH molar ratio = 26 (CH: cyclohexane). CPH was performed at 350 °C by using a H_2/CP molar ratio = 29 (CP: cyclopentane). Prior to the test reactions, catalysts were reduced "in situ" for 3 h under flowing H_2 at 350 °C. The catalyst weight used in the CHD experiments was such as to obtain a conversion lower than 5% (differential flow reactor).

Temperature-programmed reduction (TPR) experiments were performed with a H_2 (5%, v/v)–He mixture and a heating rate of 10 °C min^{-1} in a flow reactor coupled to a mass spectrometer Omnistar Baltzers for gas analysis. Approximately 0.1 g of sample was heated in an electric furnace up to 800 °C. During the TPR experiments, the mixture was passed through the reactor with a flow rate equal to 60 cm^3 min^{-1}. A pre-treatment with He at 150 °C was done for 1 h before the TPR experiments.

Hydrogen chemisorption measurements were carried out in discontinuous equipment. Samples were previously reduced at 350 °C under flowing H_2 for 3 h, evacuated at 5×10^{-5} Torr and finally cooled down to room temperature. The total H_2 chemisorption isotherm was performed at room temperature between 25 and 100 Torr.

XPS measurements were carried out in a VG-Microtech Multilab spectrometer. This equipment operates with an energy power of 50 eV (radiation Mg Kα, $h\nu$ = 1253.6 eV). The pressure of the analysis chamber was maintained at 4×10^{-10} Torr. Samples were previously reduced "in situ" with H_2 at 350 °C for 3 h (without contact with air). Binding energies (BE) of the signals were referred to the C 1s peak at 284.9 eV. Peak areas were estimated by fitting the curves with combination of Lorentzian–Gaussian curves of variable proportion.

3. Results and discussion

3.1. Carvone hydrogenation

Fig. 3 shows the results of the carvone activity versus the reaction time for C-P based catalysts, both monometallic (A) and bimetallic ones (ASn013 and ASn04). As it can be seen, the catalytic behavior of the monometallic Pt catalyst was very different to that of the bimetallic ones. In fact, when the tin loading slightly increases, the activity decreases and for the highest tin loading it is very low. These results agree with our previous results [14,15].

Table 2 shows the selectivity values of the studied catalysts measured at 1 h reaction time. The major products are: carvomenthone, unsaturated ketones (carvotanacetone and dihy-
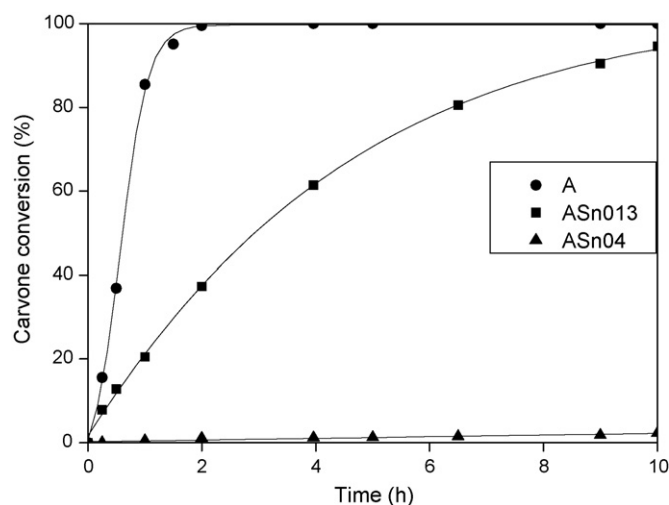

Fig. 3. Carvone conversion vs. reaction time for A and ASn catalysts.

drocarvone) and carveol, the latter sometimes in a very low quantity. As it is shown, the major products are the unsaturated ketones, mainly carvotanacetone, thus suggesting that a consecutive mechanism to carvomenthone and carvotanalcohol is not completed over these catalysts at the first hour of reaction time such as it happened with Pt catalysts supported on alumina [14]. For this C-P based catalysts, the selectivity to unsaturated ketones tends to decrease with increasing Sn loadings whereas the selectivity to carveol (the double unsaturated alcohol) increases at the initial steps of the reaction, from about 5% for the ASn013 catalyst up to about 50% for the ASn04 one. At higher reaction times, the selectivity to carveol decreases up to a 10% at 10 h of reaction time. The behavior of these PtSn catalysts supported on activated carbon powder was different from the one observed for PtSn/Al$_2$O$_3$ ones. The monometallic Pt/Al$_2$O$_3$ catalyst was very active but non-selective to unsaturated alcohols since it produced mainly saturated ketones [14]. The tin or germanium addition to Pt/Al$_2$O$_3$ increased the selectivity to unsaturated ketones and produced unsaturated alcohols in a minor proportion, mainly carvotanalcohol. It seems that the nature of the support plays an important role both in the activity and the selectivity [14,15].

Table 3 shows the results of the test reactions of the metallic phase: initial reaction rate (r_{CH}^0) and activation energy (E_{act}) values for the cyclohexane dehydrogenation (CHD), initial conversion (X_{CP}^0) for the cyclopentane hydrogenolysis (CPH) and chemisorption values expressed as H/Pt. It can be observed that the tin addition to the parent Pt catalyst, A, produces an important decrease of dehydrogenation rate. The activation energy of CH

Table 2
Selectivity (%) to different products in carvone hydrogenation with ASn catalysts measured at 1 h reaction time

Catalyst	%Sn (wt%)	Carvomenthone (%)	Unsaturated ketones (%)	Carveol (%)
A	0	9.0	90	1.0
ASn013	0.13	9.6	85.1	5.3
ASn04	0.4	13.2	47.2	49.6

Table 3
Initial reaction rate (r_{CH}^0) and activation energy (E_{act}) values of the CHD, initial conversion (X_{CP}^0) of CPH for the different catalysts and chemisorption values expressed as H/Pt

Catalyst	r_{CH}^0 (mol h^{-1} g Pt^{-1})	E_{act} (kcal mol^{-1})	X_{CP}^0 (mol h^{-1} g Pt^{-1})	H/Pt
A	32.0	20	6.8	0.39
ASn04	3.0	29	0	0.29
B	4.0	43	28.2	0.47
BSn1	4.2	44	17.1	0.32
BSn2	4.4	45	14.5	n.m.
BSn3	1.9	40	3.5	0.23
BGe1	3.3	46	14.6	0.10
BGe2	2.5	46	15.4	–
C	4.5	47	24.5	0.29
CGe1	3.9	–	18.3	0.26
CGe2	3.9	48	20.0	0.22
CGe3	3.4	48	16	–
CGe4	3.9	44	16.3	–

dehydrogenation for the ASn04 catalyst increases with respect to that of the monometallic one. It should be pointed out that the CH dehydrogenation is a structure-insensitive reaction [16] and any change in the reaction rate higher than one order of magnitude and the modification of the activation energy, indicate that an electronic interaction between both metals exists. The negligible activity of the bimetallic catalysts in the CP hydrogenolysis (a structure-sensitive reaction [17]) indicates that the concentration of ensembles of Pt atoms required for this reaction were broken by tin particles. So, from the test reactions of the metallic phase, it could be concluded that the Sn would be diluting or blocking the Pt and Pt–Sn alloy particles. In what the hydrogen chemisorption it respects, there is a lower decrease (mainly for the ASn04 catalyst) in the chemisorption values with the Sn addition than in the CH activity (see Table 3) probably due to a different structural requirements of the hydrogen chemisorption with respect to the cyclohexane dehydrogenation.

TPR results of A and ASn04 catalysts are shown in Fig. 4. It must be indicated that, according to the literature [15] the Sn/carbon catalyst prepared on the same support shows a broad and very important reduction peak at high temperature (500–800 °C) which can be attributed to a Sn reduction and also to an additional effect such as a large hydrogen retention on the carbon surface. The TPR profile of the monometallic catalyst shows a sharp peak at about 230 °C that corresponds to the reduction of the deposited Pt complex as it was evidenced from previous studies [18]. The bimetallic catalysts, ASn013 and ASn04 show two wide and large peaks, the ones at low temperature are caused by the co-reduction of deposited Pt complex and Sn [18] and the ones at high temperature can be attributed to the reaction of the hydrogen with reactive surface sites produced by the decomposition of functional surface groups [19] and reduction of Sn stabilized on the support. Thus, it can be concluded that tin can be reduced at lower temperature in the presence of Pt. Table 4 shows XPS results of A and ASn04 catalysts and it can be concluded that the surface of the ASn04 catalyst is conformed by Pt^0, Sn(II/IV) in an important proportion and placed near Pt, and small amounts of Sn^0 which could be alloyed with Pt^0. The high Sn/Pt atomic surface ratio indicates a very important Sn enrichment in the bimetallic catalyst.

It must be remembered that Sn ions placed near to surface Pt atoms, would enhance the polarization of the oxygen atom in the carbonyl group, increasing the positive charge on the carbon atom of the carbonyl group and favoring its reaction with hydrogen atoms dissociated in the neighboring Pt atoms. For the catalyst with low Sn loading (0.13 wt%), ionic tin moieties placed on the Pt would be partially inhibiting the C=C bonds hydrogenation and, in consequence, the carbonyl group would be polarized but in a small magnitude. For the ASn04 catalyst, even though the concentration of ionic Sn moieties is enough to polarize the carbonyl group (giving carveol), an important dilution effect also exists together with a blockage of Pt atoms due to the surface tin enrichment that highly decreases the catalytic activ-
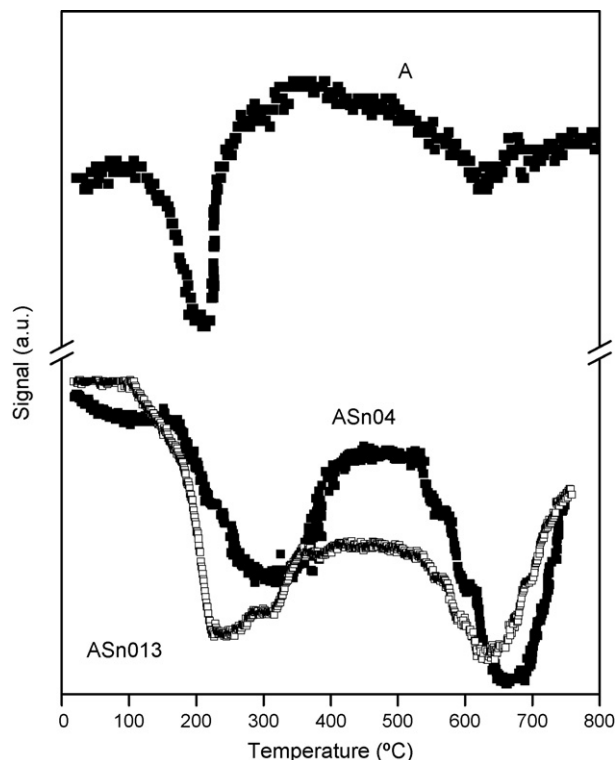

Fig. 4. TPR profiles of A and ASn catalysts.

Table 4
XPS results of the catalysts pre-reduced "in situ" at 350 °C corresponding to Pt $4f_{7/2}$ and Sn $3d_{5/2}$ levels

Catalyst	Pt^0 (%)	Sn^0 (%)	Sn(II/IV) (%)	Sn/Pt bulk atomic ratio	Sn(II/IV)/Pt surface atomic ratio
A	100	–	–	–	
ASn04	100	12	88	1.3	24
B	100	–	–	–	–
BSn1	100	19	81	0.3	1.7
BSn2	100	5	95	0.7	3.0

Percentages of each species and bulk and surface Sn/Pt atomic ratios for reduced bimetallic catalysts.

ity. Moreover, XPS results show a Sn surface enrichment, this indicating that important amounts of Sn are covering both the Pt surface and also the alloy particles. Finally, results show that the changes in the selectivity of bimetallic ASn catalysts supported on carbon with respect to the ones supported on alumina, are due not only to the action of the promoter (Sn) but the effect of the support as well [14]. As it was mentioned before, there were differences in the selectivity between the monometallic Pt/C-P and Pt/Al₂O₃ catalysts [15]. The differences between carbon and alumina as a Pt support could be attributed, for example, to differences in the metallic dispersion, in the internal distribution of the metallic phase in the catalytic particles, and in the surface chemistry of the support.

3.2. Citral hydrogenation

3.2.1. BSn series

Fig. 5 shows the results of the citral hydrogenation conversion and selectivities (defined as the ratio between the percentage of a given product and the sum of the percentages of all the products) for the two B catalyst series: BSn and BGe ones as a function of the reaction time. The obtained products are the ones seen on Fig. 2: unsaturated alcohols, UA (nerol + geraniol), citronellal, CAL, isopulegol, ISO, citronellol, COL, menthol, MEN, dimethyloctanol, DOL and very small amounts of other products like 5-caranol and α-terpenol that were omitted in Fig. 5. In our case, no acetals were found to be present among the reaction products. The catalytic activity was defined as the percentage of citral converted into all products. As it can be seen for BSn series, the catalytic activity is higher as the tin content increases. This agrees with the results of other authors [20]. In what the selectivity it is concerned, the Sn addition to Pt enhances the selectivity to unsaturated alcohols which means that the hydrogenation of the carbonyl group is preferentially favored with respect to the hydrogenation of double C=C bonds. This agrees with the results reported by Neri et al. [20] for PtSn/C catalysts and by Galvagno et al. [5,21] for RuSn/C ones. It can be seen a modification of the reaction products distribution when the Sn content increases. Thus, for the monometallic catalyst it was observed a production of unsaturated alcohols (about 40%) that increases with the reaction time, an important amount of isopulegol (which is one of the major products) mainly at the beginning of the reaction, and also citronellol, citronellal and menthol. When the Sn content increases in the bimetallic catalysts, the selectivity to unsaturated alcohols strongly increases, reaching 78% at the beginning of the reaction and about 65% at 10 h of reaction time for the cata-

lyst with the highest tin content (see Fig. 5). On the other hand, the selectivity to citronellal and menthol are negatively affected by the tin addition as well as the isopulegol production. The cyclization reaction to give isopulegol and menthol is catalyzed by the acidic sites of the support and these sites could be poisoned by tin moieties. It should be indicated that other authors found a poisoning effect of Sn on the acidic sites of alumina [22], which would be responsible for the higher inhibition of the cyclization reaction when the Sn content increases.

It can be observed from Table 3 that the initial reaction rate in CHD is sligthly modified when the Sn content increases. Besides, the activation energy in the CHD remains practically unmodified (±5% with respect to the value corresponding to the monometallic sample) by the addition of Sn. The very low modification of both the activation energy and the initial CHD activity as the Sn content increases would indicate a negligible electronic modification of Pt by Sn or a low Pt–Sn alloy formation. Besides, the initial activity of the CPH reaction is slightly modified for the PtSn catalyst with 1 and 2 wt% Sn and the X^0_{CP} decreases about one order of magnitude for the catalyst with the highest tin loading. So, there might be a low decrease of the concentration of the Pt ensembles necessary for this reaction. However, this effect seems to be very different from the one observed in PtSn/C-P catalysts with lower metal loadings such as ASn ones, where it was observed a very important modification of both the activity (in CHD and CPH) and E_{act} values in CHD. In conclusion, the Sn addition to B slightly modifies electronically the metallic phase and only decreases the concentration of the hydrogenolytic Pt ensembles for the catalyst with the highest tin loading. Thus, the metallic surface could be conformed by fractions of Sn partially intercalated among Pt species, in a way that the concentration of hydrogenolytic sites would be diminished and also there would be a fraction of oxidized Sn placed over the support, according to the decrease of isopulegol formation.

The conformation of the metallic surface can be better understood by analyzing the TPR profiles of B, BSn2 and BSn3 catalysts shown in Fig. 6. Bimetallic PtSn/C-P catalysts show important differences respect to the monometallic Pt/C-P and Sn/C-P ones (see the above comment about the TPR of the Sn/Carbon catalyst [15]). In the bimetallic samples there is a peak at low temperatures (at about 200–350 °C) probably due to Pt reduction and to a simultaneous catalytic effect of Pt on the Sn reduction. This peak at low temperature also appears in the zone of Pt reduction in the monometallic catalyst which also displays a wide and small peak of hydrogen consumption at high tem-
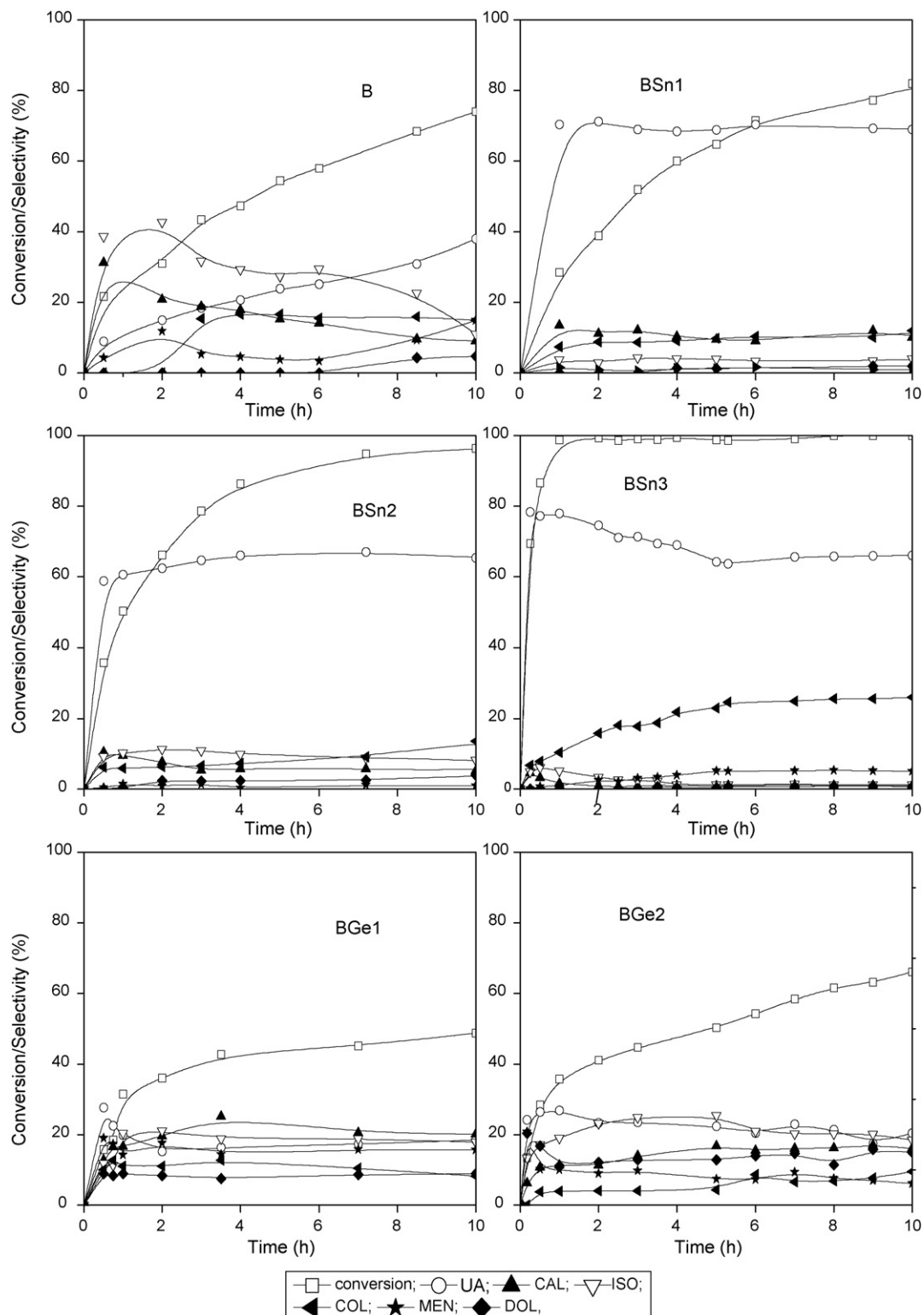
Fig. 5. Citral conversion and selectivity to the different products vs. reaction time for B, BSn and BGe catalyst series.

peratures. This peak in the monometallic Pt catalyst, as it was discussed for the A series, could be attributed to the reaction of hydrogen with reactive sites of the support that are left by the thermal desorption of functional groups. The bimetallic catalysts present a hydrogen consumption peak at about 550–700 °C due to the reduction of reactive sites caused by the release of func-

tional groups of the support (that desorb CO) and probably to a concomitant partial reduction of a fraction of free Sn stabilized on the support.

Table 4 shows the XPS results (the percentage of the species with different oxidation states, the Sn/Pt bulk atomic ratios and Sn/Pt surface atomic ratios) of BSn catalysts previously reduced
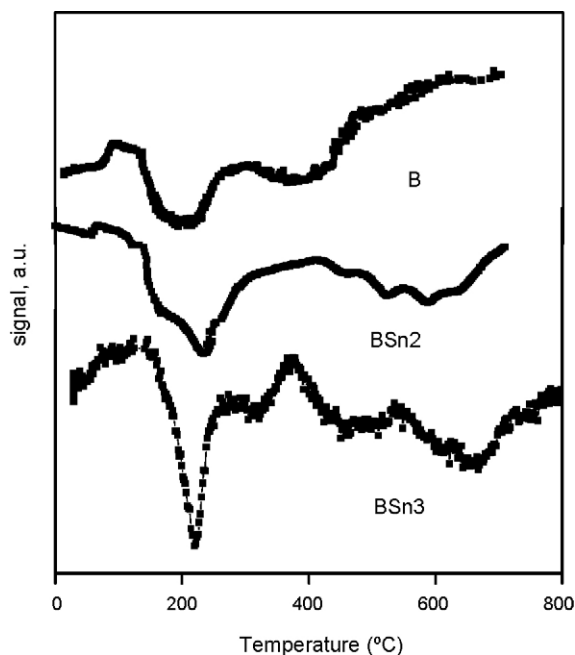
Fig. 6. TPR profiles of B and BSn catalyst series.

Fig. 7. Yield to unsaturated alcohols (UA) vs. reaction time for the BSn1 catalyst with different solvents.

"in situ" at 350 °C. It can be concluded that the reducibility of Sn decreases as its content increases. Besides, by comparing the bulk atomic Sn/Pt ratios with the corresponding surface atomic Sn/Pt ones, it can be inferred that there is a certain surface enrichment of the metallic phase in Sn. However, this Sn enrichment is much lower than the one found for the ASn04 catalyst. Hence, the structure of the metallic phase can be modified by the metallic loading.

From Table 3 it can be seen the results of the hydrogen chemisorption. The tin addition decreases the hydrogen chemisorption capacity for BSn series, the tendency being similar to the one found for the activity in the CHD.

Taking into account both the results in the selective hydrogenation of citral and that the zerovalent Sn percentage decreases when the Sn loading increases, it could be inferred that the selectivity for the hydrogenation of the carbonyl group giving unsaturated alcohols seems to increase when the Sn oxidized/Pt surface atomic ratio increases for the catalyst series. Besides, Homs et al. [23] reported that the Sn has a positive effect on the selectivity to unsaturated alcohols, which could be explained as due to the polarization of the oxygen atom of the carbonyl group by ionic Sn species and to a partial dilution of Pt atoms by Sn ones. This last effect would inhibit the hydrogenation of the double C=C bonds and the adsorption of the unsaturated alcohols such as it will be discussed later. So, the Sn addition to the Pt/C-P catalyst would not produce an important electronic modification of the metallic phase (low alloy formation) and it would slightly decrease the hydrogenolytic capacity.

In order to study the effect of the solvent on both the activity and the selectivity to unsaturated alcohols, three tests using 2-propanol, 2-pentanol and *tert*-butanol as solvents were achieved for the BSn1 catalyst. As it can be observed in Fig. 7, by using the more branched solvent, the lowest yield to UA is
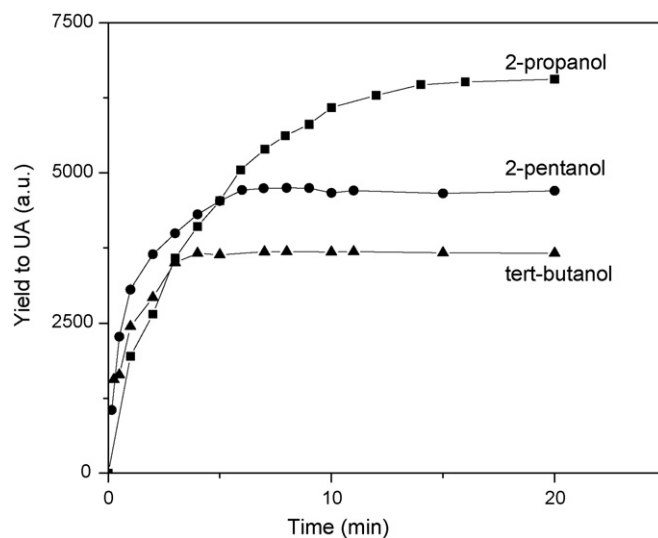
clearly achieved. It seems that probably the molecules of this branched solvent would cover the metallic surface of the catalyst and would avoid or hinder the adsorption of the carbonyl group. It seems that probably the molecules of *tert*-butanol would cover in an important proportion the metallic surface of the catalyst and would avoid or hinder the adsorption of the carbonyl group.
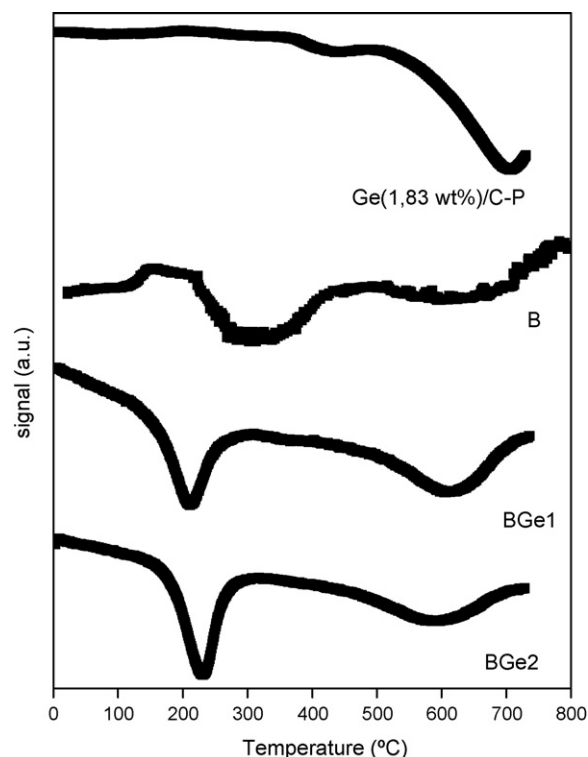

Fig. 8. TPR profiles of B, Ge(1.83 wt%)/C-P and BGe catalysts.

3.2.2. BGe series

Fig. 5 also shows the activity and the selectivity to the different products of the BGe series. As it can be seen, this series is less active and also less selective to unsaturated alcohols than the BSn one. From the test reaction results (Table 3), it can be seen that the Ge addition to Pt slightly decreases the initial reaction rate of the CHD, whereas the activation energies slightly increase from 43 kcal mol^{-1} (B catalyst) to 46 kcal mol^{-1} (BGe1 and BGe2 catalysts), and the initial conversion in the CPH also slightly decreases. Besides, the chemisorption values of the bimetallic catalysts are much lower than the one of the monometallic catalyst. Thus, there might be a certain electronic interaction between Pt and Ge and a probable alloy formation. Besides, the decreased hydrogenolysis activity values indicate a small decrease of the concentration of the Pt ensembles by the Ge addition.

The TPR profiles of the monometallic Ge(1.83 wt%)/C-P, B, BGe1 and BGe2 catalysts are shown in Fig. 8. The monometallic Ge catalyst shows a large peak with a maximum at about 700 °C (see Fig. 8) due to both the Ge reduction and also the decomposition of functional groups of the support that desorb CO and retain H$_2$. The bimetallic catalysts show two well-defined peaks, one at about 230 °C that can be attributed to the Pt–Ge co-reduction and another one at approximately 600 °C due to the decomposition of the functional surface groups and the partial reduction of free Ge species placed on the support. Hence, the increase of the activation energy in CHD and the presence of the well-defined peak at low temperatures in TPR for BGe catalysts indicate that a fraction of Ge is interacting with Pt in these catalysts, with probable alloy formation. Besides, an important fraction of Ge species would be located over the support, such as TPR shows
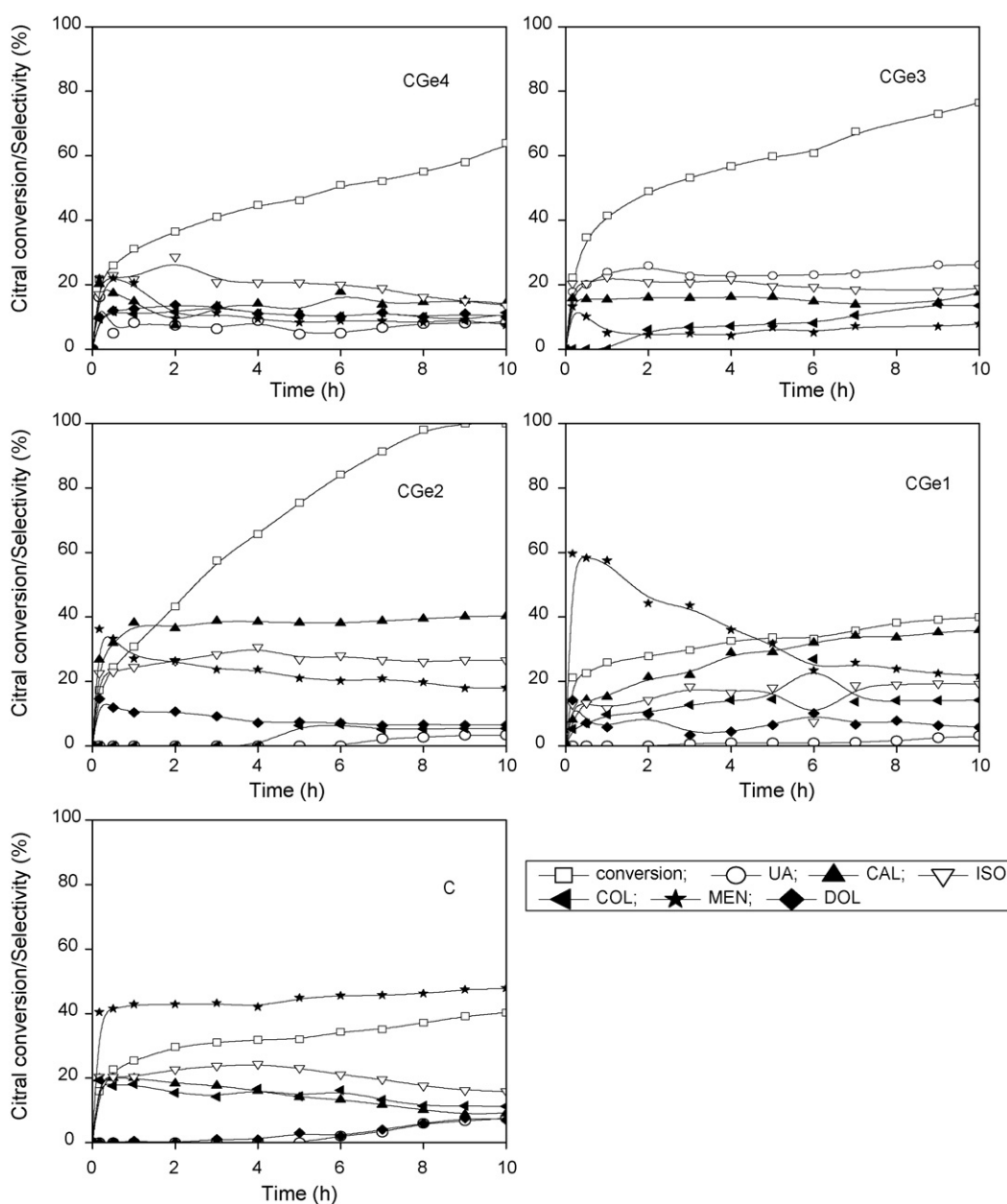

Fig. 9. Citral conversion and selectivity to the different products vs. reaction time for C and CGe catalyst series.

(Fig. 8). In conclusion, very few oxidized Ge species would be placed near Pt in order to polarize the carbonyl group of the citral molecule, and this would be the reason for the low selectivity to UA of these BGe catalysts.

3.2.3. CGe series

Fig. 9 shows the results of the citral hydrogenation (activity and selectivity) versus the reaction time. There is a maximum in the activity when the Ge loading increases, whereas the UA selectivities were low, e.g. a maximum value of 26% was reached for the CGe3 catalyst. It is worth noting that the good selectivity to menthols shown by the monometallic catalyst (and also for the catalyst with the lowest Ge loading) would probably be caused by the high concentration of acidic sites of the carbonaceous support that catalyze the isopulegol cyclization. This effect was not seen in the bimetallic catalysts because Ge species would poison the acidic sites of the carbon, avoiding the cyclization reaction to give isopulegol and then menthols. Mazzieri [24] found that Ge decreases the acid strength distribution of alumina in bimetallic PtGe/Al₂O₃ catalysts used for naphtha reforming.

From the test reaction results shown in Table 3, it can be evidenced that the initial reaction rate in CHD slightly decreases when the Ge content increases. Besides, the activation energy in the CHD remains practically unmodified. The very low modification of both the activation energy and the initial activity in CHD as the Ge loading increases, would indicate no electronic modification of Pt by Ge. The activity in CPH also slightly decreases when increasing amounts of Ge are added to Pt. This behavior can be explained as due to a small decrease of the concentration of the Pt ensembles necessary for this reaction when Ge is added to Pt. Moreover, when the second metal is added to Pt, there is a gradual decrease of the hydrogen chemisorption.
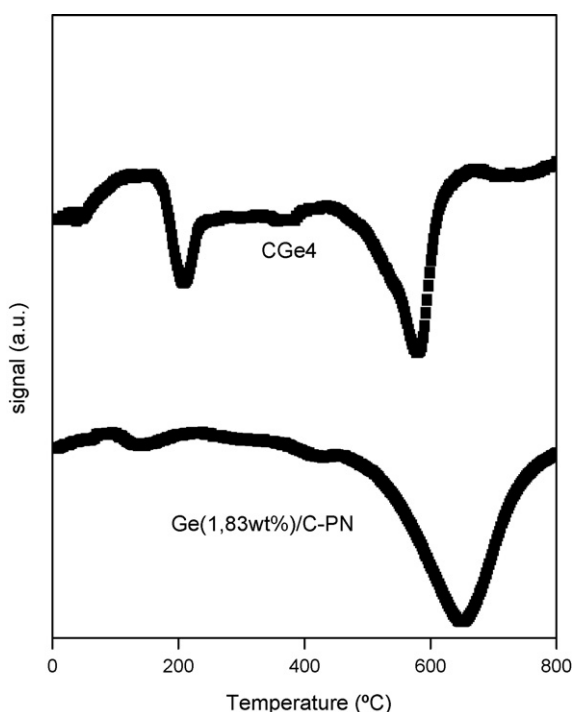

Fig. 10. TPR profiles of Ge(1.83 wt%)/C-PN and BGe3 catalyst.

Fig. 10 shows TPR profiles of C-PN based catalysts, viz., CGe4 and the monometallic Ge(1.83 wt%)/C-PN catalyst. The monometallic catalyst shows a large peak at high temperature, which can be assigned to both Ge reduction and decomposition of functional groups that desorb CO at very high temperature (higher than 500 °C) whereas the bimetallic catalyst shows a sharp and large peak at about 200 °C due to the Pt–Ge co-reduction and a broad hydrogen consumption zone (500–650 °C) which could be due to the reduction of free Ge oxides species and to the decomposition of functional groups of the support. There seems to be free Ge on the support since the peaks at the Ge reduction zone are rather large.

In this CGe catalyst series, Ge would be mainly located over the support without modifying either electronically or geometrically the Pt sites, except for the catalyst with the highest Ge/Pt atomic ratio that shows a dilution effect. Hence, in these catalysts, the polarization of the carbonyl group is practically negligible, thus leading to very low selectivities to nerol and geraniol (UA).

4. Conclusions

- PtSn/CP catalysts show good performance for the selective hydrogenation of citral to UA.
- The tin addition to Pt(1 wt%)/C decreases the activity but it increases the selectivity to unsaturated alcohols in the carvone hydrogenation reaction. The surface of the reduced ASn catalyst is conformed by metallic platinum, Sn(II) and/or Sn(IV) species, and also tin in the zerovalent state that would be forming alloys with zerovalent platinum. The presence of oxidized Sn species would polarize the carbonyl group of the carvone molecule, favoring its hydrogenation to carveol.
- When the tin content in the bimetallic Pt(5 wt%)Sn/C-P increases, the selectivity to UA (in the citral hydrogenation reaction) strongly increases, reaching a maximum value of about 80%.
- On the other hand, PtGe catalysts supported on carbon purified and functionalized with nitric acid do not show a good selectivity to unsaturated alcohols during the citral hydrogenation. The low concentration of Ge species that would be placed near Pt to polarize the carbonyl group of the citral molecule could be responsible for this behavior that is different from the one shown by PtSn catalysts.
- The used of branched solvents, like *tert*-butanol, leads to a decrease in the yield to nerol and geraniol (UA) during the citral hydrogenation and this could be due to that the molecules of this branched solvent would cover the metallic surface of the catalyst, thus hindering the adsorption of the carbonyl group.

Acknowledgements

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