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The Influence of the Preparation Method on the Behaviour of PtGe Catalysts Supported on Activated Carbon in Citral Hydrogenation

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Abstract The liquid-phase citral hydrogenation carried out over PtGe catalysts prepared by different techniques and supported on activated carbon powder purified and functionalized with nitric acid (C-PN) was investigated. In catalysts prepared by conventional successive impregnation (CI), Ge does not improve in an important way either the activity or the selectivity to unsaturated alcohols. Besides, PtGe catalysts prepared by controlled surface reaction (CSR) show much better activities and selectivities to unsaturated alcohols (UA). It is needed a large concentration of Ge to polarize the carbonyl group in the case of CI catalysts because Ge is located mainly over the support and small quantities would be deposited over the Pt particles. In PtGe catalysts prepared by CSR, Ge moieties would polarize the carbonyl group since they would be placed near PtGe nanoclusters, thus giving high selectivity to UA.

Keywords PtGe/C catalysts · Catalyst preparation · Citral hydrogenation · Activated carbon support

1 Introduction

The citral (3,7-dimethyl-2,6-octadienal) molecule has been chosen as a model to study the performance of PtGe catalysts supported on granular carbon. The hydrogenation of the carbonyl group of citral is thermodynamically less favored than the hydrogenation of double C=C bonds so, most of studies try to selectively enhance the hydrogenation of the carbonyl group to produce nerol and geraniol [1–3] and minimize the production of unwanted minor products such as the acetals [4]. The acetalization is a side reaction between the solvent and the carbonyl group of the citral molecule catalyzed by acidic sites of the support. According to the literature [4], the acetalization can be avoided if branched solvents are used, that is why isopropanol was used as a solvent in this work. The reaction scheme of citral hydrogenation is displayed in Fig. 1.

The hydrogenation of unsaturated α–β aldehydes has been widely studied using not only different mono and bimetallic systems but also different supports [1–6]. The products of these reactions are important intermediates in pharmaceutical and perfumery industries [1–3]. The nature of the metallic phase of the catalyst and the support influences the activity and selectivity in the hydrogenation of unsaturated α–β aldehydes [1, 3, 5]. Besides, the use of bimetallic catalysts could modify the activity and improve the selectivity to unsaturated alcohols [3].

The functionalization of an activated carbon consists on increasing the number of oxygen-containing groups. The study of the oxygenated surface groups on carbons has received much attention even though its influence on the catalytic behaviour of the carbon supported catalysts has not been completely elucidated yet [7]. It is very well known that several types of surface functional groups (phenolic, carboxylic, carbonyls, anhydrides, etc.) can be

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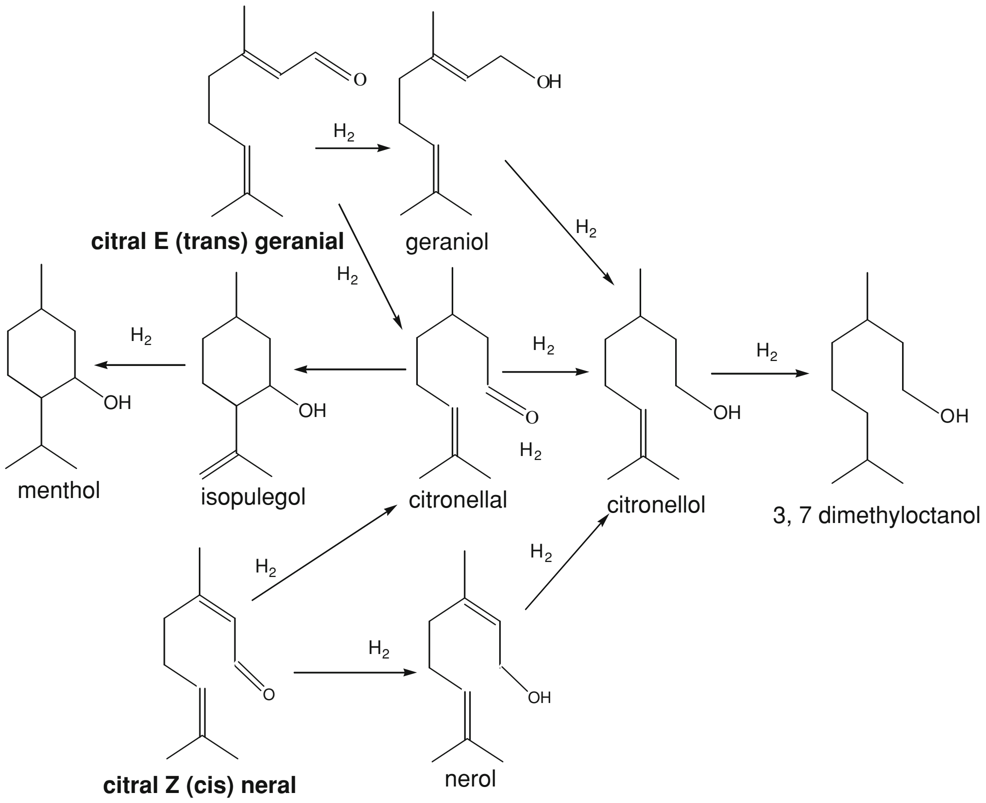

Fig. 1 Reaction scheme of citral hydrogenation

produced as a consequence of the oxidation treatments. These groups can act as anchorage sites of the metallic precursor, favoring both the wetting of the carbon and the impregnation with polar solutions [8]. Some authors [8, 9] found that when the concentration of surface oxygen groups increases, the metal dispersion decreases, but others [10] have not found any correlation between the concentration of acidic sites and the catalytic activity or the sintering effect [11].

It has been demonstrated that in the case of supported transition metal catalysts modified by germanium there are several methods which provide a close contact between the noble metal and the modifier. The selective modification of catalytically active phase can only be achieved by (i) "redox-type" surface reactions [12] and (ii) use of Controlled Surface Reactions (CSRs) [13, 14].

CSRs between metal tetraalkyls (M′–R4) and adsorbed hydrogen have been first described in the early eighties [15, 16]. The surface chemistry [17, 18] involved in the two-step anchoring modification can be described by the following equations, the step being (i) germanium anchoring (reaction (1)), and (ii) decomposition of surface organometallic complexes formed (reaction (2)).

$$MH_{ads} + M'R_4 \rightarrow M - M'R_3 + xRH \qquad (1)$$

$$M - M'R_3 + (4 - x)/2H_2 \rightarrow M - M' + (4 - x)RH \qquad (2)$$

Reaction between hydrogen adsorbed on the metals (MH_{ads}) (M = Pt, Rh, Ru and Ni) and $M'R_4$ (M′ = Ge, Sn, Pb, Se, Zn and R = CH_3, C_2H_5, C_4H_9) proceeds via stepwise hydrogenolysis of the M′–R bond with the formation of a Primary Surface Complexes (PSC) and elimination of RH (see reaction (1)). Upon properly chosen conditions, reaction (1) results in direct metal-metal interaction, which can be maintained during the decomposition in a hydrogen atmosphere of formed PSC (reaction (2)). Upon using this approach the modifier is introduced almost exclusively into the parent metal.

In our earlier computer modeling studies it has been demonstrated [18] that, upon using $Sn(C_2H_5)_4$ as a modifier, depending on the particle size of platinum and the number of alkyl groups left in PSC, at monolayer coverage, Sn/Pt_s ratio was in the range of 0.3–0.6.

As emerges from earlier studies, the high content of tin resulted in highly selective Pt catalysts for the hydrogenation of crotonaldehyde to crotylalcohol [19]. In order to obtain high M′/M ratios, new anchoring sites should be created. The M′/M ratio can be increased substantially using the following reaction conditions (see reaction (1)) [18, 20]: high initial M'_o/M_s ratio (where M'_o is the initial amount of modifier used in the anchoring step and M_s is the total number of surface metal atoms); increased reaction temperature (T_r); long reaction time; carrying out reaction

(1) in the presence of hydrogen; and addition of oxygen during anchoring reaction (1).

In this paper it is reported a study of PtGe catalysts supported on activated carbon powder prepared by different techniques. The PtGe series were prepared on carbon purified and subsequently functionalized with nitric acid. Besides, two preparation techniques were used for preparing PtGe catalysts: a conventional impregnation (first Pt, second Ge) and controlled surface reaction. It must be indicated that for the citral hydrogenation in liquid phase, very few studies [21, 22] were reported over the PtGe system supported on purified and functionalized carbon The catalysts were characterized by temperature programmed reduction, TPR, H_2 chemisorption and test reactions of the metallic phase (cyclohexane dehydrogenation, CHD and cyclopentane hydrogenolysis, CPH), XPS, isopropanol dehydration and measurements of equilibrium pH.

The objective of this work is to correlate preparation methods of bimetallic catalysts with their physicochemical characteristics and their catalytic performance in citral hydrogenation and also to find the ways to increase the amount of germanium anchored onto the platinum and to maintain the overall control of Ge anchoring, i.e. to suppress the amount of germanium introduced onto the support.

2 Experimental

2.1 Support

It was used a commercial granular activated carbon derived from a pit of peach (GA-160 from Carbonac) with a final particle size between 100 and 140 mesh, the textural properties being $S_{\mathrm{BET}} = 987\ \mathrm{m}^2\ \mathrm{g}^{-1}$ and $V_{\mathrm{micropore}} = 0.33\ \mathrm{cm}^3\ \mathrm{g}^{-1}$ and it was called as “C”. The support was 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 supports were repeatedly washed with deionized water up to a final pH = 4. After the HF treatment, they were washed with deionized water up to the same pH of the water used for washing, and then dried at 120 °C. In order to eliminate sulphur compounds, the acid-treated carbonaceous material was submitted to a thermal treatment under flowing hydrogen ($5\ \mathrm{mL\ min}^{-1}\ \mathrm{g}^{-1}$) at 850 °C for 8 h. After the purification treatment, the impurity content was markedly reduced, from 2.9 wt% to 0.16 wt% and the sulphur content was undetectable, as it was shown by EDX determinations [9, 23]. Then, a functionalization treatment with an aqueous solution of HNO_3 was achieved. This treatment was carried out at 25 °C for 48 h. The concentration of the HNO_3 solution was 10 wt%. The support was called “C-PN”. After the functionalization treatment, the samples were dried at 120 °C overnight.

The surface area of the carbon support ($987\ \mathrm{m}^2\ \mathrm{g}^{-1}$) and the porous volume ($0.33\ \mathrm{cm}^3\ \mathrm{g}^{-1}$) remain unmodified after the purification ($976\ \mathrm{m}^2\ \mathrm{g}^{-1}$ and $0.33\ \mathrm{cm}^3\ \mathrm{g}^{-1}$, respectively) and they are slightly modified ($876\ \mathrm{m}^2\ \mathrm{g}^{-1}$ and $0.29\ \mathrm{cm}^3\ \mathrm{g}^{-1}$) by the functionalization treatment with HNO_3 as de Miguel et al. [24] and Torres et al. [9] reported.

2.2 Preparation of the Catalysts

2.2.1 Conventional Impregnation (CI)

The monometallic Pt catalyst was prepared by conventional impregnation of the supports with an aqueous solution of H_2PtCl_6. The total amount of Pt in the impregnating solution was such as to obtain a final Pt loading (nominal) of 5 wt%. The catalyst precursors were dried at 120 °C, overnight. PtGe (CI) catalysts were prepared by successive impregnation with a solution of $GeCl_4$, the nominal Ge loadings being 0.08, 0.22 and 0.61 wt%. In all cases, impregnations were carried out at 25 °C for 6 h, using a volume of impregnation solution/mass of support ratio of $30\ \mathrm{mL\ g}^{-1}$, and stirring rate of 600 rpm. Table 1 shows the characteristics of the studied catalysts, the parent catalyst (Pt/C-PN) was called B and the bimetallic ones were: BGe1CI, BGe2CI and BGe3CI.

2.2.2 Controlled Surface Reactions (CSRs)

The surface controlled reactions were done from a parent Pt(5wt%)/C-PN catalyst, (that was called B) previously reduced at 300 °C for 1 h, by using germanium tetraethyl, ($Ge(C_2H_5)_4$) as a germanium precursor. Characteristic features of these catalysts are also summarized in Table 1.

Prior to the germanium anchoring step, the parent Pt catalyst was reduced under flowing hydrogen at 350 °C for 2 h. After reduction, the catalyst was cooled to room temperature in the H_2 flow and then purged with argon for 30 min. Next, the catalyst was transferred into a glass reactor without exposure to air and slurred with deoxygenated solvent (*n*-hexane or *n*-decane).

Table 1 Characteristics of Pt supported catalysts

Catalyst	Pt (wt%)	Ge (wt%)	(Ge/Pt) atomic
Pt/C-PN (B)	5	–	–
BGe1CI	5	0.08	0.04
BGe2CI	5	0.22	0.12
BGe3CI	5	0.61	0.33
BGe1SR	5	0.08	0.04
BGe2SR	5	0.22	0.12
BGe3SR	5	0.68	0.37

The first step of germanium anchoring was investigated using a 151 mL stirred glass reactor equipped with rubber septum to take samples from gas phase. The germanium anchoring was carried out in *n*-hexane at 55 °C or *n*-decane at higher temperature ($T = 100$ and 155 °C) in a hydrogen atmosphere for 4 h. In the Ge anchoring step the solvent volume was 15 mL and the amount of the parent supported Pt catalyst was 1 g. Upon achieving the required reaction temperature the germanium anchoring was started by injection of appropriate amount of $Ge(C_2H_5)_4$ into the slurry.

When the anchoring reaction (1) was completed, the catalyst was washed at 50 °C four times with hexane to remove unreacted germanium tetraethyl. When surface reaction (1) was carried out in *n*-decane, the catalyst was washed once with pure *n*-decane followed by a four time-washing with *n*-hexane at 50 °C. Then the catalyst was dried in vacuum (5 Torr) for 2 h at the same temperature to remove the trace of solvent used in the previous step.

Reaction (2), i.e., the decomposition of formed surface organometallic species was carried out in hydrogen atmosphere by Temperature Programmed Decomposition (TPD) technique (experimental parameters: heating rate = 5 °C min^{-1}, hydrogen flow rate = 30 cm^3 min^{-1}, amount of catalyst = 0.3–0.5 g).

The germanium anchoring process was monitored by determination of the amount of ethane formed both during the germanium anchoring step (reaction (1)) and the decomposition of surface organometallic complexes (reaction (2)) by GC using a 3 m long Al_2O_3 column at 100 °C. A correction was done for the amount of ethane dissolved in the solvents used.

The so-prepared catalysts were designated as BGe1SR, BGe2SR and BGe3SR.

2.3 Characterizations

2-propanol dehydration experiments were performed at 225 and 300 °C and at 1 atm in a continuous flow reactor. Prior to the reaction, samples were reduced “in situ” with H_2 at 350 °C. The alcohol was vaporized in a H_2 stream (H_2/2-propanol molar ratio = 19) and fed to the reactor with a space velocity of 0.52 mol alcohol h^{-1} g cat^{-1}. The sample weight was 100 mg.

The measurement of the equilibrium pH of activated carbons (with and without Ge) were performed by putting in contact the solid (1 g, 35/80 mesh) with 100 mL of deionised water at room temperature according to the technique reported by Roman-Martınez et al. [8].

Test reactions of the metallic phase were carried out in a flow reactor. Cyclohexane dehydrogenation (CHD) was carried out at 250 °C by using a H_2/CH molar ratio = 26, CH: cyclohexane. Cyclopentane hydrogenolysis (CPH) was performed at 320 °C by using a H_2/CP molar ratio = 29; CP: cyclopentane. Prior to the test reactions, catalysts were reduced “in situ” under flowing H_2 at 320 °C for 3 h. The reaction products were benzene for CHD and *n*-pentane for CPH. The catalyst weight used in the CHD experiments was such as to obtain a conversion lower than 5% (differential flow reactor). In the case of the CPH reaction, the cyclopentane conversions under these conditions were clearly higher than 5%, in consequence, the behavior of the reactor was far from the differential flow reactor model except for the SR series, so the calculation of the initial reaction rates was not possible.

Hydrogen chemisorption measurements were carried out in discontinuous equipment. Samples were previously reduced at 320 °C under flowing H_2 for 3 h, evacuated at 5×10^{-5} Torr and finally cooled down to room temperature. The H_2 adsorption isotherm was performed at room temperature between 0 and 100 Torr.

Catalysts were also characterized by temperature-programmed reduction (TPR) by using 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 the gas analysis. The sample (0.1 g) was heated in an electric furnace up to 800 °C. During the TPR experiments, the reductive mixture flowed through the reactor with a rate of 60 mL min^{-1}. A pre-treatment with He at 150 °C was done for 1 h before the TPR experiments.

XPS measurements were carried out in a VG-Microtech Multilab spectrometer, which operates with an energy power of 50 eV (radiation MgKα, hν = 1253.6 eV). The pressure of the analysis chamber was kept at 4×10^{-10} Torr. Samples were previously reduced “in situ” at 350 °C with H_2 for 2 h.

The citral hydrogenation was carried out in discontinuous equipment with a device for sampling the reaction products. The reaction was done at 70 °C and atmospheric pressure. Pure isopropanol was used as a solvent. The volume of solvent, the citral amount (Sigma, 61% cis-and 36% trans-) and the weight of catalysts were 30 mL, 0.30 mL, and 0.30 g, respectively. Prior to the reaction, catalysts prepared by CI were reduced “in situ” under flowing H_2 at 350 °C for 3 h whereas the ones prepared by CSR were treated with N_2 at 120 °C for 1 h and then reduced at 320 °C, 3 h. The reaction mixture was stirred at 1,400 rpm and the products were analyzed in a GC chromatographic system by using a Supelcowax 10 M column and a FID as a detector. The detected products were the ones seen in Fig. 1 and also minor products (α-terpenol, 5-caranol). From previous experiments, diffusional limitations were found to be absent under these conditions [25].

3 Results and Discussion

3.1 Germanium Anchoring by CSRs

The influence of the temperature of the surface reaction (1) on the amount of germanium anchored was investigated in the temperature range of 55–155 °C. In order to achieve high germanium content, it was used a very high initial concentration of $Ge(C_2H_5)_4$ (see the column of Ge_0/Pt_s in Table 2). Data related to the reaction rates and material balance of germanium anchoring at three different reaction temperatures are summarized in Table 2.

As emerges from Table 2 both the rate of formation of surface complexes (w_0) and the amount of germanium anchored onto platinum (Ge/Pt_s) are proportional to the reaction temperature used (T_r). It can be seen that the stoichiometry x ($x = 4n^{I}/(n^{I} + n^{II})$) and the amount of ethane formed during the surface reaction (1) (n^{I}) increases while the amount of ethane formed during decomposition reaction (2) (n^{II}) decreases in increasing temperature of anchoring reaction.

The values of x (see Table 2) are in the range of 0.62–3.77 and strongly depend on the temperature of germanium anchoring. As emerges from Table 2 upon increasing the temperature of anchoring T_r, the amount of germanium anchored per surface Pt atom (Ge/Pt_s) increases up to 1.24.

Due to the high stability of Ge–C bond, low value of x ($x = 0.62$) and an unusually low activity at $T_r = 55$ °C was observed (Table 2). The low value of x ($x < 1$) indicates that surface organometallic complexes formed should contain both-$Ge(C_2H_5)_4$ and-$Ge(C_2H_5)_3$ type surface species. At low temperature, the surface reaction (1) probably takes place only on energetically more active Pt sites (kink and corner sites). In this case $Ge(C_2H_5)_4$ type surface species, i.e., strongly adsorbed precursor compound onto platinum, are the main surface entities formed. In this experiment (catalyst BGe1SR), the final germanium coverage is below the monolayer ($Ge/Pt_s = 0.15$).

In our earlier studies it has been demonstrated that the excess of hydrogen strongly increases the amount of alkyl groups involved in reaction (1) [18, 20]. Consequently, in this case the exact separation of the anchoring and decomposition steps cannot always be achieved and high values of stoichiometry of surface reaction (1) can be expected.

When the surface reaction (1) was carried out at $T_r = 105$ °C, the high value of x ($x = 3.18$) would show that surface species with only one alkyl group-$Ge(C_2H_5)$ should be present. The formation of "naked" Ge ($x = 4.0$) in minor amount can also be suggested. In this experiment a germanium coverage lower than the monolayer is achieved, i.e., the ratio of Ge/Pt_s in the formed alloy type supported Ge–Pt catalysts is 0.40 (see Table 2).

As Table 2 shows, the value of Ge/Pt_s increases up to 1.24 and extremely high values of x ($x = 3.77$) was obtained at $T_r = 155$ °C. Values of $x \geq 3.0$ show that surface modification at high temperatures ($T_r = 105$ and 155 °C) should result in coordinatively unsaturated moieties-$Ge(C_2H_5)$ and "naked" Ge anchored exclusively to the platinum. The formation of "naked" germanium in surface reaction (1) can result in an additional feature. This form of Ge can present on the platinum surface as naked adatoms and migrate into the bulk of platinum and form alloy type species either at the surface or the bulk phase even during the anchoring reaction.

It was shown [26] that the surface hydroxyl groups of different supports (SiO_2, Al_2O_3 or SiO_2–Al_2O_3) reacts irreversibly with $Ge(n\text{-}C_4H_9)_4$ at about 250 °C, resulting in the release of one butyl ligand per grafted germanium and formation of highly thermal stable (up to 400 °C) grafted complex-$OGe(n\text{-}C_4H_9)_3$ ($x = 1.0$). Consequently, due to the high stability of Ge–C bond, only in the presence of platinum the high extent of loss of the alkyl groups in the first step of germanium anchoring ($x \geq 3.0$) can be proposed.

Moreover the temperature used for catalysts modification ($T_r = 55$–155 °C) was not high enough for the interaction of $Ge(C_2H_5)_4$ with surface groups of support. For this reason the anchoring of germanium organic moieties onto the support in the SR series of catalysts can be excluded. A similar result has been reported by Crabb and

Table 2 General data related to germanium anchoring

Catalyst	T_r (°C)	Solvent	Ge_0/Pt_s	w_0[a]	n^{I} [b]	n^{II} [c]	x	Ge wt%[d]	Ge/Pt_s[e]
PtGe1-SR	55	Hexane	36.0	0.3	7.1	38.8	0.62	0.08	0.15
PtGe2-SR	105	Decane	35.5	2.7	98.4	25.4	3.18	0.22	0.40
PtGe3-SR	155	Decane	41.2	20.0	350.8	21.7	3.77	0.68	1.24

[a] Initial rate of germanium anchoring in reaction (1), (mol g_{cat}^{-1} × min × 10^{-6})

[b] Amount of ethane formed in reaction (1) (mol g_{cat}^{-1} × 10^{-6})

[c] Amount of ethane formed in reaction (2) (mol g_{cat}^{-1} × 10^{-6})

[d] Germanium content calculated from the material balance of germanium anchoring

[e] Amount of germanium anchored per surface Pt atom, calculated using H_2 chemisorption data ($H/Pt_s = 0.29$)

Ravikumar [27] for the deposition of Ge atoms on Pt/C catalysts using surface organometallic chemistry (SOMC) techniques. No reaction was observed for the blank reaction between the carbon support and the Ge(n-C_4H_9)$_4$, indicating that there was a selective reaction between the Pt surface and the Ge precursor.

The comparison of the reactivity of germanium surface organometallic species (extent of the dealkylation during anchoring) on platinum and surface of different supports indicates that, under condition of surface reaction (1), direct anchoring of germanium organic moieties onto the support can be neglected.

3.2 Test Reactions of the Metallic Phase and XPS

Table 3 shows the initial reaction rate (r^0_{CH}) for the cyclohexane dehydrogenation (CHD). Since the activity in the CHD reaction was practically constant throughout the reaction time for the range of used temperatures (200–300 °C), the initial reaction rates (r^0_{CH}) were calculated as the average ones ($r^0_{CH} = x/(W/F^0_{CH})$, where x: CH conversion, W: Pt weight in the sample, F^0_{CH}: molar CH flow).

Figure 2 shows the initial conversions (x^0_{CP}) for the cyclopentane hydrogenolysis (CPH) versus the Ge/Pt atomic ratio and Fig. 3 shows the cyclopentane conversion versus time, the curves being fitted by exponential functions and the deactivation parameter, Δ, was defined as (Xo − Xf)/Xo (where X_0 and X_f are the initial and final CP conversions, respectively).

The initial reaction rate in CHD slightly decreases when the Ge content increases for the CI series. Taking into account the structure-insensitive character of the CHD reaction [28], it can be inferred that the very low modification of the initial activity as the Ge loading increases for the BGeCI series, would indicate no electronic modification of Pt by Ge. On the other hand, in the case of the BGeSR series, when the amount of Ge added to Pt increases, there is an important decrease of the CHD rate. This fact would indicate an electronic modification of Pt by Ge addition, with probable alloy formation, or a side-blocking effect of Ge on Pt sites. In order to obtaing more information about the state of the metallic phase of these SR catalysts, bimetallic BGe3SR catalyst were characterized by XPS, but it was not possible obtain a well defined spectra corresponding to Ge3d signal due to the low Ge concentration (0.68 wt%, maximum Ge loading). However Pt 4f signals could be observed at 72.1 eV, thus indicating the presence of Pt in zerovalent state. The peak for Pt° appears at binding energies that are somewhat higher than those observed in the monometallic Pt/C catalyst (71.5 eV for Pt^0 in the reduced catalyst). If one assumes that platinum is in the zerovalent state in the bimetallic catalyst after the reduction treatment, the higher values of the BE's should be attributed to a kind of electronic modification of the surface platinum atoms,

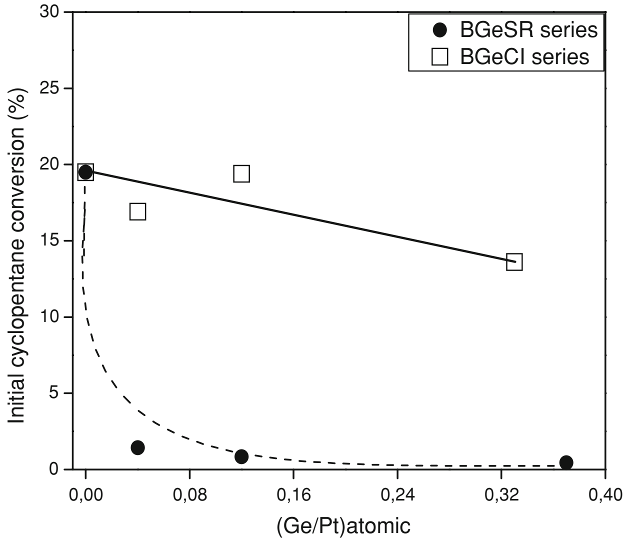

Fig. 2 Initial cyclopentane conversion versus (Ge/Pt) atomic ratio for the two catalyst series

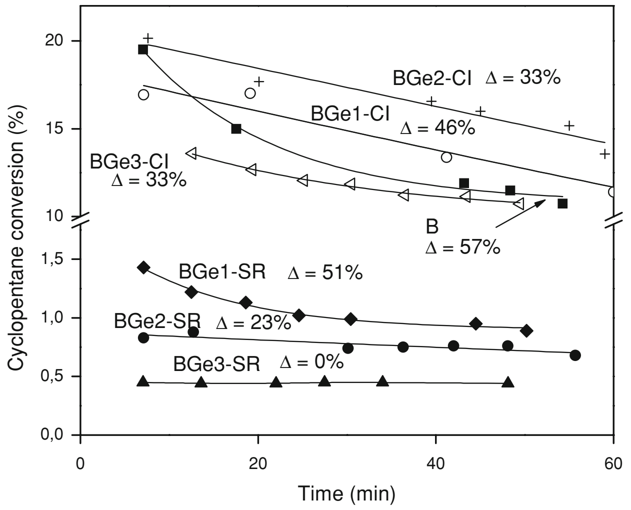

Fig. 3 Cyclopentane conversion versus reaction time for the different catalysts

Table 3 Initial reaction rate (r^0_{CH}) of the cyclohexane dehydrogenation for the different catalysts

Catalyst	r^0_{CH} (mol h^{-1} g Pt^{-1})
B	4.50
BGe1CI	3.90
BGe2CI	3.90
BGe3CI	3.40
BGe1SR	3.96
BGe2SR	2.20
BGe3SR	0.56

such as proposed by Coloma et al. for bimetallic PtSn/C catalysts [29]. Similar results were found for the Pt–Ge/$Al_2 0_3$ system [30] and were explained on the basis of a more electrodeficient state for platinum in the bimetallic catalyst. On the other hand, the Pt 4f7/2 peak in the bimetallic Pt–Re/SiO_2 was found at a slightly larger binding energy as compared to monometallic Pt/SiO_2 and this was attributed to an effect of Pt–Re alloy formation, which could lead to an electronic modification of the surface platinum atoms [31]. Besides, Crabb and Ravikumar [27] carried out a study of carbon supported PtGe electrocatalysts (with very high metal concentrations), which were prepared using surface organometallic chemistry and then they were reduced at low temperatures (200 °C). In these conditions they found an important interaction between the platinum and germanium supported by the hydrogen chemisorption results.

It can be also observed from Fig. 2 that the activity in CPH reaction (structure-sensitive reaction [32]) decreases but not in a very important degree when increasing amounts of Ge are added to Pt for the BGeCI series. 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 by conventional impregnation. In the case of the BGeSR series, the CPH activity is noticeably decreased, this indicating a high dilution effect of Pt by Ge addition, even at very low Ge/Pt atomic ratios.

Figure 3 depicts that the Ge addition, in general, reduces the deactivation capacity for the CI catalyst series, whereas SR catalysts, as it was mentioned, have very low activities.

3.3 Hydrogen Chemisorption

Figure 4 shows the hydrogen chemisorption values versus the Ge/Pt atomic ratio. It can be observed that when Ge is added to Pt by the CSR method, the chemisorption capacity drastically decreases (also for the catalyst with the lowest Ge concentration), whereas when the second metal is added to Pt by CI, there is a gradual decrease of the hydrogen chemisorption upon increasing the Ge/Pt atomic ratio, the tendency being similar to that of the CPH activity.

These results indicate that only in CSR catalysts, Ge would be in an intimate contact with Pt, thus modifying both electronically and geometrically the metallic phase.

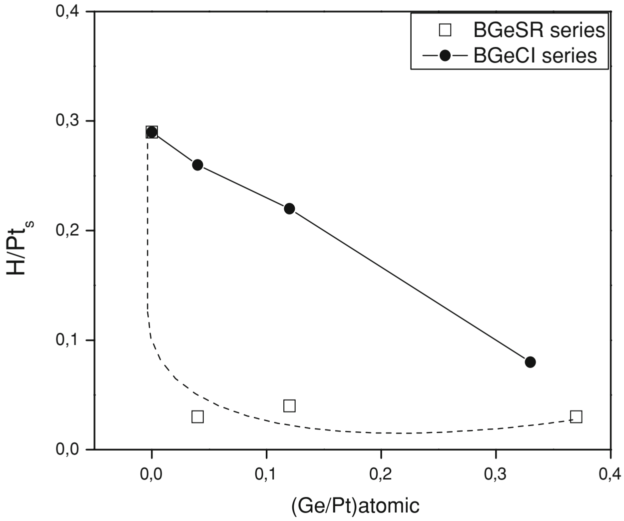

Fig. 4 H/Pts versus (Ge/Pt) atomic ratio for the two catalyst series

3.4 TPR Results

Figure 5 shows TPR profiles of C-PN based catalysts, viz., BGe3CI, BGe3SR and the monometallic Ge(1.83 wt%)/C-PN catalyst. The last one shows a large peak of both Ge reduction and decomposition of functional groups that desorb CO at very high temperature (higher than 600 °C) whereas the bimetallic catalyst prepared by CI shows a sharp and large peak at about 230 °C (due to the Pt reduction or 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 as the peaks at the Ge reduction zone are rather large.

The TPR profile of the BGe3SR catalyst (Fig. 5) does not show any reduction peak at low temperature that is in the zone of Pt or PtGe reduction, because the catalysts

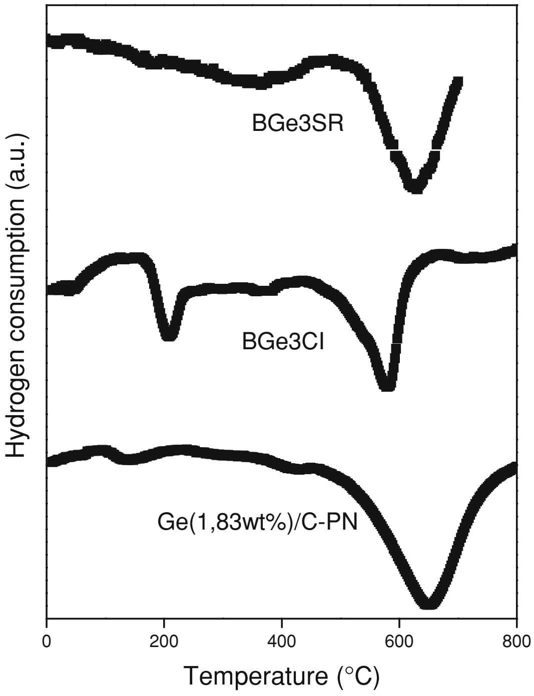

Fig. 5 TPR profiles of BGe3CI, BGe3SR and Ge(1.83wt%)/C-PN catalysts

prepared by CSR were previously reduced during the preparation procedure. This profile shows a broad peak at temperature higher than 600 °C, corresponding mainly to the decomposition of functional groups of the carbon, and in a minor extension to the reduction of a small fraction of free Ge oxide species which did not interact with Pt during the surface reaction.

3.5 Citral Hydrogenation

Figure 6 shows both the activity and the selectivity values to unsaturated alcohols (UA), citronellal (CAL), isopulegol (ISO) and citronellol (COL), menthol (MEN) and 3,7-dimethyloctanol (DMOL) for B and BGeCI catalysts versus the reaction time. The catalytic activity was defined as the percentage of citral converted into all products and the selectivity was defined as the percentage of a given product with respect to all the products. In this case, there seems to be a growing tendency in the activity when the Ge loading increases whereas the UA selectivities are very low. It is worth noting that the good selectivity to menthols showed by the monometallic catalysts (of about a 50%) would probably be caused by the high concentration of acidic sites of the carbonaceous support that catalyze the cyclization to isopulegol. This effect was not seen in the bimetallic catalysts because Ge species would poison the acidic sites of the carbon [33]. Mazzieri et al. found that Ge produces a modification of the acid strength distribution of alumina in bimetallic PtGe catalysts supported on alumina used for naphtha reforming. The poisoning effect of the acidic sites of the support the Ge produces would be lower than the one done by Sn species since the selectivities to isopulegol are higher for PtGe catalysts than for PtSn ones [25, 34]. In order to characterize the acid properties of mono and bimetallic catalysts (prepared by conventional impregnation-CI-) supported on the functionalized activated carbons and to confirm the effect of Ge addition on the acidity of the carbon, we carried out experiments consisting of 2-propanol dehydration reaction at atmospheric pressure, which were performed in a continuous flow reactor. Figure 7 shows that the initial dehydration rates for the monometallic Pt/C catalyst at 225 and 300 °C are much higher than the ones for the bimetallic catalyst (BGe3CI) at the corresponding temperatures. This fact indicates that Ge addition produces a poisoning effect on the acid sites of the functionalized carbon. Besides, measurements of the equilibrium pH of activated carbons (with and without Ge) were performed and the results indicate a modification of the equilibrium pH from 5.5 for the HNO_3-functionalized carbon (C-PN) to 7.1 for a Ge (1.83 wt%)/C-PN, which is in agreement with results of dehydration experiments and confirms the inhibition of the acid sites of the carbon by Ge addition using the CI method.

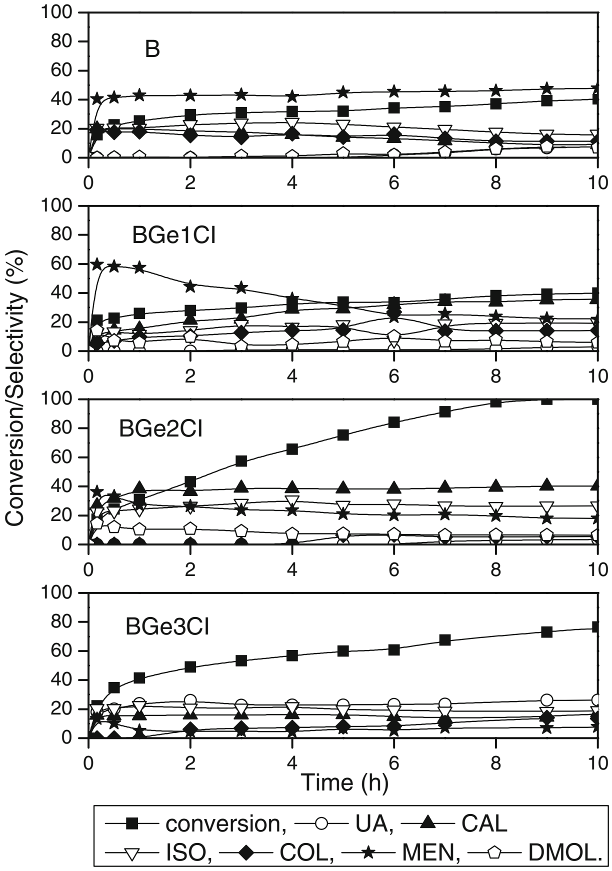

Fig. 6 Citral conversion and selectivity to the different products versus reaction time for BGeCI series. U.A.: unsaturated alcohols, CAL: citronellal, ISO: isopulegol, COL: citronellol, MEN: menthol, DMOL: dimethyloctanol

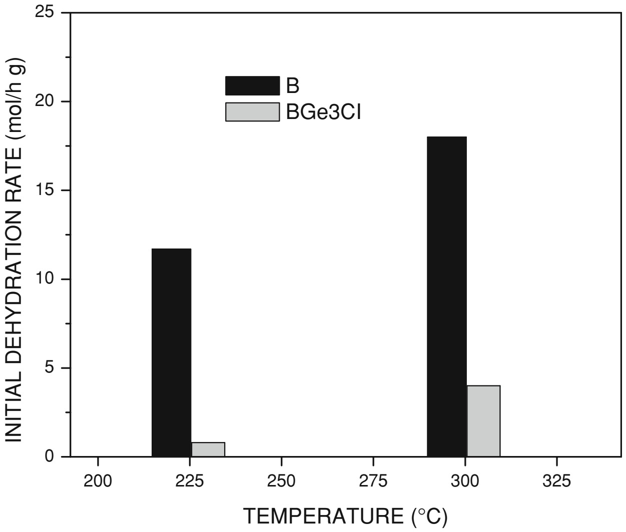

Fig. 7 Initial 2-propanol dehydration rates for B and BGeCI catalysts at 225 and 300 °C

In conclusion over CI type catalysts the cyclization can take place due to the formation of citronellal and its transformation into isopulegol over acidic sites of the support. Upon increasing the amount of germanium introduced partly onto the support the cyclization reaction is suppressed. On the other hand, over SR type catalysts, the route for the cyclization is almost fully ceased due to the suppression of the formation of citronellal, the key intermediate involved in cyclization, such as it will be analyzed later. This finding indicates that the Ge is not deposited onto the support.

Figure 8 shows the conversion and selectivity values for the series of catalysts prepared by CSR, BGeSR ones. In this case, the SR series showed a very good activity respect to the CI series and also respect to the parent monometallic catalyst (B). There exists an optimum Ge content that maximized the catalytic activity for the BGe2SR catalysts, this reaching the 100% conversion at 1 h reaction time and, in this condition, the UA selectivity reached 60%, and then the concentration of UA (nerol and geraniol) began to decrease since they reacted to give citronellol and subsequently, 3,7 dimethyloctanol. So, when comparing the two BGe series (the one prepared by conventional impregnation and the other one by CSR), it was found that SR catalysts were more active (mainly BGe2SR) and much more selective to UA than CI ones. In this sense, Fig. 9 shows the influence of Ge/Pt atomic ratio on the selectivity values to UA (obtained at the highest conversion) for the two series. It is observed that for the SR series, there is a pronounced increase of the selectivity to nerol and geraniol, even at low Ge/Pt atomic ratios. According to the catalytic behavior of CSR catalysts, the citral conversion seems to depend on $\mathrm{Ge_{anchored}/Pt_s}$ ratios. Taking into account the different results obtained for both series in citral hydrogenation, it can be concluded that the preparation by controlled surface reaction would lead to an intimate contact between Pt and Ge but the CI preparation method would not produce this effect. From TPR, test reactions and chemisorption measurements, it can be concluded that in the case of CI catalysts, Ge would be mainly located over the support with minor modifications either electronic or geometric of the Pt sites, except for the catalyst with the highest Ge/Pt atomic ratio that shows a dilution effect. Hence, in these CI catalysts, the polarization of the carbonyl group is practically negligible, thus leading to very low selectivities to nerol and geraniol (UA).

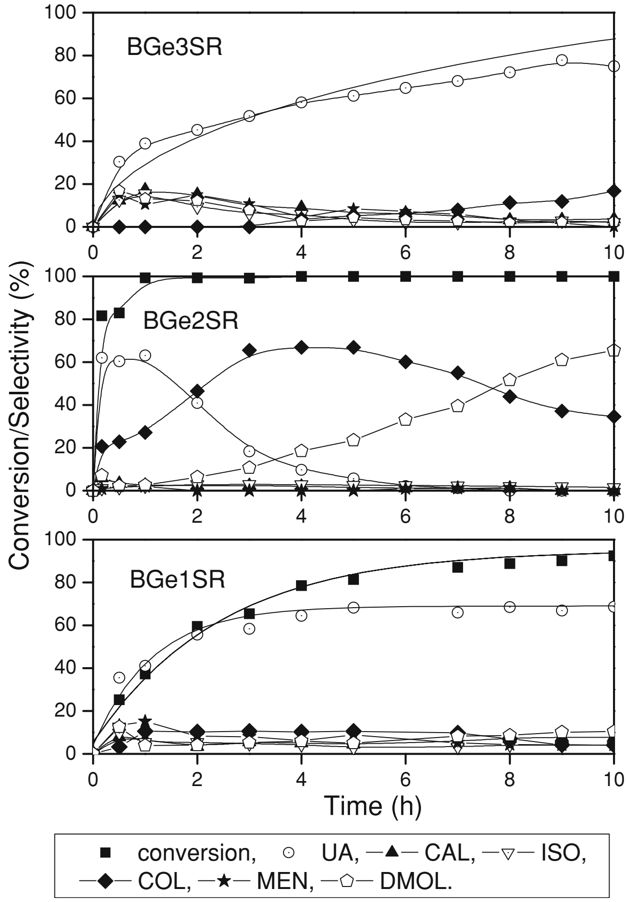

Fig. 8 Citral conversion and selectivity to the different products versus reaction time for BGeSR series. U.A.: unsaturated alcohols, CAL: citronellal, ISO: isopulegol, COL: citronellol, MEN: menthol, DMOL: dimethyloctanol

In the case of SR catalysts, the preparation technique leads to a metallic phase with an important PtGe interaction. The presence of Pt and Ge in an intimate contact, with probable alloy formation, together with oxidized Ge species (that polarize the carbonyl group of the citral) in the vicinity of the metallic phase, is responsible for the improved selectivity to unsaturated alcohols.

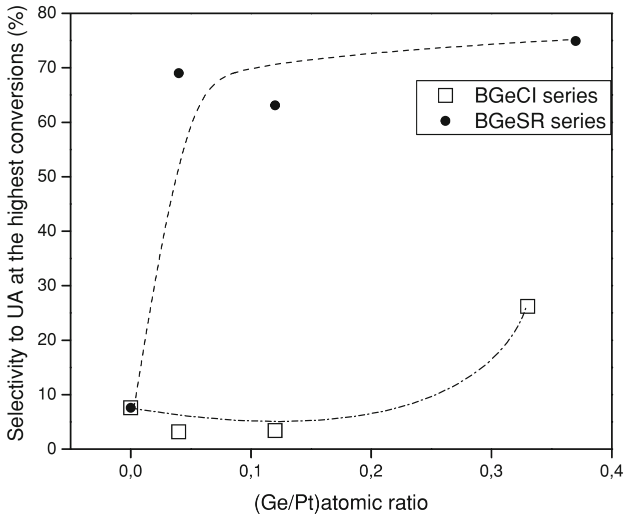

Fig. 9 Selectivity to unsaturated alcohols (UA) measured at the highest conversion versus the (Ge/Pt) atomic ratio for the two catalyst series

4 Conclusions

It is well known that the selective hydrogenation of the carbonyl group and the inhibition of the hydrogenation of C=C bonds of citral would require a particular structure of the metallic surface [5]. In the case of PtGe catalysts prepared by CI, the Ge is placed over the support and it would not polarize the carbonyl group since it would not be located very close to it. From these results it could be concluded that the Ge does not promote the polarization of the carbonyl group in these type of catalysts. On the other hand, the preparation of the catalysts by controlled surface reaction leads to an intimate contact between Pt and Ge, with probably alloy formation, and the presence of ionic forms of Ge would activate the carbonyl group of the citral molecule. Besides, the dilution of Pt sites by metallic Ge would avoid the re-adsorption of the formed unsaturated alcohols.

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