

Effect of the support in Pt and PtSn catalysts used for selective hydrogenation of carvone

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Abstract

In this paper, a study on the hydrogenation of carvone by using Pt/Al₂O₃, PtSn/Al₂O₃, PtGe/Al₂O₃, Pt/C and PtSn/C is reported. TPR, H₂ chemisorption, XPS and test reaction results show that the addition of a second metal to Pt leads to important modifications of the structure of the metallic phase, though these modifications are different according to the nature of the support (Al₂O₃ or C). The activity and selectivity of these catalysts in carvone hydrogenation depend not only on the composition of the metallic phase, but also on the nature of the support. Thus, adding Sn or Ge to Pt/Al₂O₃ enhances the selectivity to unsaturated ketones (at a fixed carvone conversion, $X_{\text{carv}} = 1$). When Pt is supported on activated carbon, small amounts of unsaturated alcohols are observed. The Sn addition to Pt/C sharply enhances the selectivity to carveol formation (the doubly unsaturated alcohol) reaching values close to 100% at the initial stages of the reaction. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The selective hydrogenation of organic molecules having different functional groups able to be hydrogenated is one of the main goals in synthesis processes for fine chemistry [1]. An interesting case is observed in the carvone molecule (terpenic monocyclic ketone), since it has three different functional groups which can be hydrogenated: one –C=O group, and two –C=C– groups (endocyclic and exocyclic ones), which display different chemical reactivities for hydrogenation. The

selective hydrogenation of –C=C– groups produces saturated and unsaturated ketones, while the selective hydrogenation of the –C=O group of carvone could produce unsaturated alcohols, products more valuable than ketone products. Fig. 1 shows the reaction scheme of the carvone hydrogenation.

The use of supported bimetallic catalysts such as Pt–Co, Pt–Ru, Pt–Sn, Pt–Ga, Rh–Sn and Pt–Ge for selective hydrogenations of α,β unsaturated aldehydes and ketones (such as crotonaldehyde, acrolein, cinnamaldehyde, citral, methyl vinyl ketone, etc.) has been extensively studied during the last years [1–5]. However, few papers about the use of supported mono- and bimetallic systems (such as Pt, Rh, Pt–Au and PtSn) for the selective hydrogenation of carvone have been reported in the literature [6–9]. Among bimetallic

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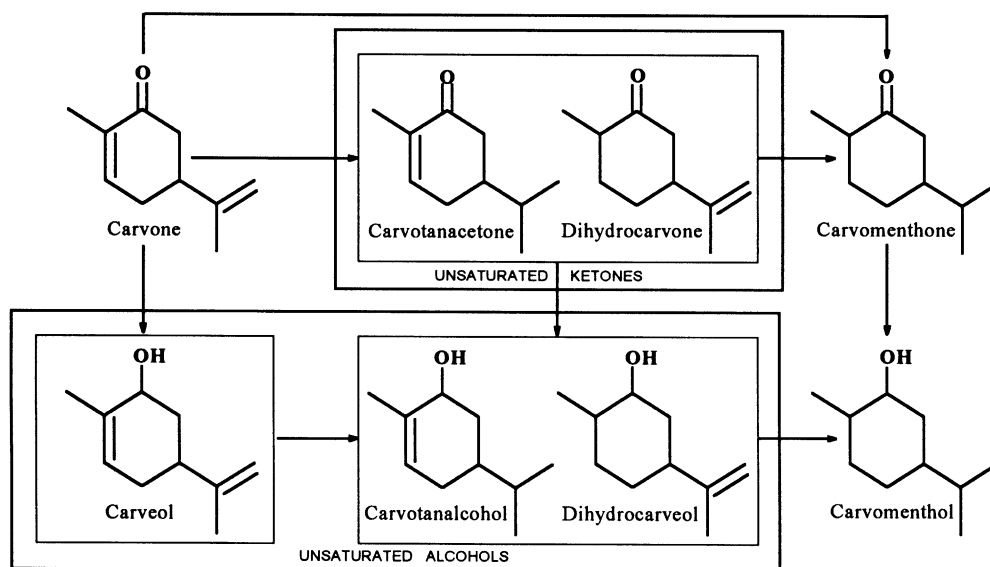


Fig. 1. Reaction scheme of the carvone hydrogenation.

catalysts, Pt–Sn appears as a very interesting one. In this sense, several authors found that both the Sn amount added to Pt and the preparation method play an important role in the selective activation of the carbonyl group during the hydrogenation of α,β unsaturated aldehydes and ketones. For these catalysts, the selectivity to different products can be modified by changing the support type, the metal particle size and by metals addition to the active phase [2]. In this paper, a study of the effect of the support and the composition of the metallic phase of Pt-based catalysts in the hydrogenation of carvone is reported.

2. Experimental

Two supports were used: a commercial γ - Al_2O_3 (CK-300 from Cyanamid Ketjen) with an $S_{\text{BET}} = 190 \text{ m}^2 \text{ g}^{-1}$, and a purified activated carbon (pit of peach carbon from Carbonac, GA-160) functionalized with H_2O_2 solution, 20% (v/v), at 298 K) with an $S_{\text{BET}} = 900 \text{ m}^2 \text{ g}^{-1}$ and an ash content of 0.2 wt.%.

The metallic phases were Pt, Pt–Sn and Pt–Ge for Al_2O_3 , and Pt and Pt–Sn for carbon. Monometallic-supported catalysts were prepared impregnating the supports with an aqueous solution of H_2PtCl_6 .

Bimetallic catalysts were prepared by successive impregnation (first with Pt and second with Sn or Ge) (SI) and co-impregnation (Co). H_2PtCl_6 , SnCl_2 (in hydrochloric solution) and GeO_2 were the metallic precursors. After impregnation, catalysts supported on alumina were dried at 393 K and then calcined at 773 K, while the catalysts supported on carbon were only dried at 393 K. The Sn/Pt molar ratio in $\text{PtSn}/\text{Al}_2\text{O}_3$ ranged between 0.32 and 0.65, and the Ge/Pt molar ratio in $\text{PtGe}/\text{Al}_2\text{O}_3$ was modified between 0.42 and 0.99. In the case of PtSn/C catalysts the Sn/Pt molar ratio was 0.82. In all cases, the Pt content was constant and equal to 1 wt.%.

The state of the metallic phase of catalysts were studied by TPR, H_2 chemisorption, X-ray photoelectron spectra (XPS) and test reactions (cyclohexane dehydrogenation). XPS were obtained by using a Fisons ESCALAB MkII 200 R spectrometer fitted with a Mg $\text{K}\alpha$ (1253.6 eV) source operated at 12 kV and 10 mA and a spherical electron analyzer. XPS measurements were carried out on samples previously treated in situ with H_2 (at 773 K for $\text{PtSn}/\text{Al}_2\text{O}_3$ and at 623 K for PtSn/C). The ion pumper analysis chamber was maintained below 10^{-9} Torr during the data acquisition. Peak areas were estimated by calculating the integral of each peak after the subtraction of the

S-shaped background and fitting the experimental peak by Lorentzian–Gaussian mix. Binding energies were referenced to C 1s peak at 284.9 eV.

The H₂ chemisorption measurements were carried out at 298 K in a volumetric equipment. The catalyst was reduced with H₂ at 773 K (PtSn/Al₂O₃) and at 623 K (PtSn/C) during 4 h, then it was outgassed under high vacuum (10⁻⁴ Torr) at 623 K (or 773 K) for 1 h. When the sample was cooled down to room temperature, the chemisorption test begun.

The catalytic activity for cyclohexane (CH) dehydrogenation was determined at atmospheric pressure in a differential flow reactor by using a H₂/CH molar ratio of 29 and a CH molar flow of 0.056 mol h⁻¹. The activation energy of this reaction was obtained by measuring the catalytic activity at 543, 558 and 573 K. The sample weight used in these experiments was the appropriate to obtain a CH conversion lower than 7%. The reaction products were only benzene and *n*-pentane for the first and second reaction, respectively. The products of both reactions were analyzed by using a gas chromatographic system.

The carvone hydrogenation reaction was carried out at 313 K and atmospheric pressure in a discontinuous volumetric reaction equipment, by using toluene as a solvent and a stirring rate of 360 rpm. In each experiment, 0.09 g of carvone dissolved in 30 cm³ of toluene was hydrogenated by using 0.40 g of catalyst. Reaction products were intermittently withdrawn from the reactor and analyzed in a GC chromatographic system with a capillary column (Supelcowax 10 M). Before reaction, catalysts supported on Al₂O₃ were reduced under flowing H₂ at 773 K, while those supported on carbon were reduced with H₂ at 623 K.

3. Results and discussion

Figs. 2–4 show the TPR profiles corresponding to PtSn/Al₂O₃-Co, PtGe/Al₂O₃-SI and PtSn/C-SI catalysts, respectively. The TPR of PtSn/Al₂O₃ catalysts show an important main reduction zone with a maximum at 523 K, in the same region that occurs the Pt reduction in the monometallic Pt/Al₂O₃ catalyst. Besides, the small reduction shoulder, observed at the region above 723 K where the Sn reduction in the monometallic Sn/Al₂O₃ is produced, indicates a

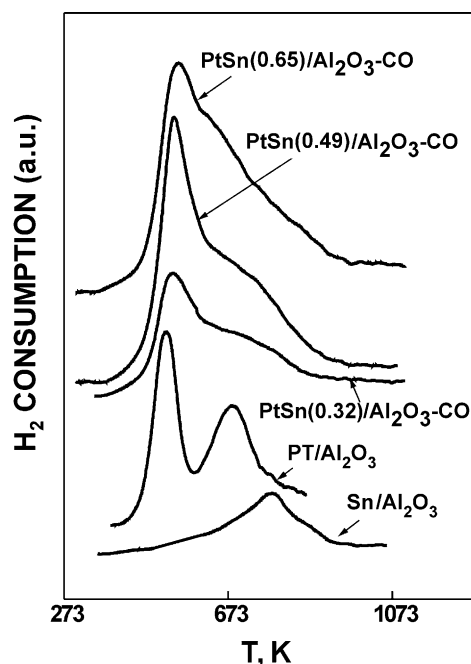


Fig. 2. TPR profiles of PtSn/Al₂O₃, Pt/Al₂O₃ and Sn/Al₂O₃ catalysts.

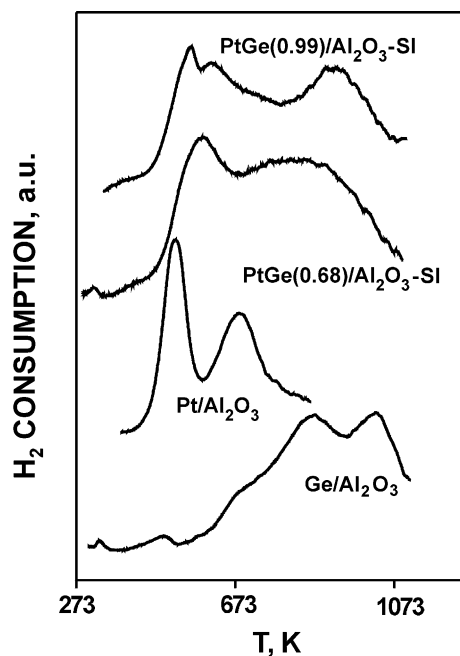


Fig. 3. TPR profiles of PtGe/Al₂O₃, Pt/Al₂O₃ and Ge/Al₂O₃ catalysts.

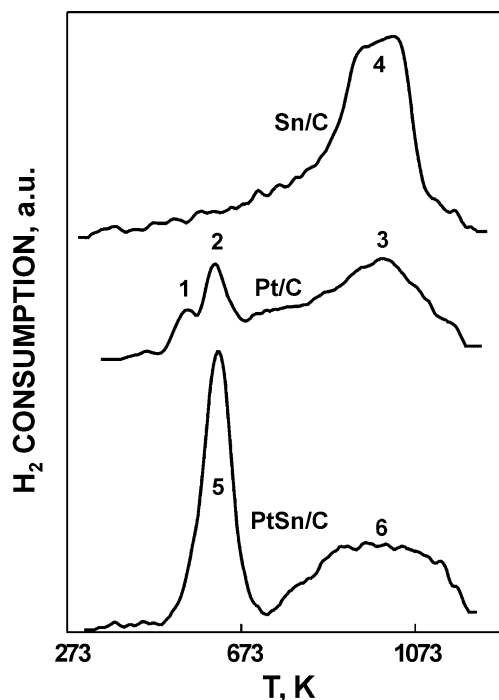


Fig. 4. TPR profiles of PtSn/C, Pt/C and Sn/C catalysts.

strong interaction between both metals, with probable alloys formation.

TPR profiles of PtGe/Al₂O₃ catalysts (Fig. 3), compared with those of the monometallic Pt/Al₂O₃ and Ge/Al₂O₃ samples, would show a lower interaction between both metals than that observed for PtSn/Al₂O₃ catalysts. In this sense, an important reduction zone at high temperature due to the Ge reduction can be seen in both PtGe/Al₂O₃ catalysts.

TPR profiles of the bimetallic PtSn/C catalyst show important differences with respect to those of the monometallic Pt/C and Sn/C catalysts (Fig. 4). The existence of a sharp peak at low temperatures (peak 5) could be due to a co-reduction of Pt and Sn. This peak appears in the zone of the Pt reduction (peak 1) in the monometallic Pt/C catalyst. Peak 2 in the TPR profile of Pt/C is due to the reaction of hydrogen with the reactive sites of the support, originated from the CO₂ thermal desorption. Peak 6 observed in the TPR profile of PtSn/C is similar to peak 3 (appearing in TPR of Pt/C). It must be noted that the TPR profile of the support without metals also shows a reduction peak similar to peak 6. Hence, peak 6 can be assigned to the reduction of functional groups of the carbon. It must be indicated that the reduction of Sn in Sn/C leads to a very large TPR reduction peak at high temperature, coinciding with the reduction zone of functional groups of the support. By comparing the TPR profiles reported in Fig. 4, it can be concluded that Sn would be in an intimate contact with Pt, without detecting the presence of free Sn species.

Table 1 shows the results of chemisorbed H₂, initial reaction rates in cyclohexane dehydrogenation and surface composition (Sn/Pt_{XPS}) of the metallic phase (determined by XPS) for the different catalysts. It can be observed that bimetallic catalysts supported both on alumina and on activated carbon show an important decrease of the CH dehydrogenation reaction rate with respect to the corresponding monometallic ones. In all cases this effect is accompanied by an important increase of the activation energy in this reaction. Taking into account the structure-insensitive character of the cyclohexane dehydrogenation [10], any

Table 1

Amounts of chemisorbed H₂ (H_I), initial reaction rates (*r*₀) at 573 K and activation energies (*E*_{CH}) in cyclohexane dehydrogenation

Sample	(M/Pt) _{mol} ^a	H _I (μmol/g)	<i>r</i> ₀ (mol/(h g Pt))	<i>E</i> _{CH} (kcal/mol)	Sn/Pt _{XPS} ^b
Pt/C	0	9.7	86.2	21.6	–
PtSn/C–Co	0.82	4.9	9.9	30.1	23.3
PtSn/C–SI	0.82	6.1	7.7	26.1	27.0
Pt/Al ₂ O ₃	0	27.6	52.3	19.1	–
PtSn/Al ₂ O ₃ –Co	0.65	3.4	12.1	30.0	3.0
PtSn/Al ₂ O ₃ –SI	0.65	3.9	11.7	29.0	–
PtGe/Al ₂ O ₃ –SI	0.68	–	24.3	26.0	–

^a M: Sn or Ge.

^b Sn/Pt_{XPS} represents the surface atomic ratio measured by XPS.

modification of the activation energy can be assigned to changes in the nature of the metallic phase due to the addition of the second metal to Pt, which could lead to alloy formation. Moreover, the lower H₂ chemisorption capacity in the bimetallic catalysts with respect to those of the monometallic ones can also be related to modifications in the structure of the metallic phase.

XPS results showed in Table 1 (data of Sn/Pt surface atomic ratios) are indicative of a strong surface enrichment of Sn in the metallic phase for PtSn/C samples. In fact, the Sn/Pt surface atomic ratio in PtSn/C samples is 10-fold higher than that corresponding to PtSn/Al₂O₃, indicating an important difference in the structure of the metallic phase when carbon is used as a support instead Al₂O₃.

Table 2 shows the distribution of the reaction products (expressed as selectivity) in the hydrogenation of carvone for Pt/Al₂O₃, Pt/C, PtSn/Al₂O₃ and PtGe/Al₂O₃ catalysts. These selectivity values to the different products were measured at the moment when the carvone is totally converted. These results indicated that Pt/Al₂O₃ is a very active but non-selective catalyst, since it produces mainly carvomenthone (the saturated ketone) and a small fraction of unsaturated ketones. The formation of unsaturated alcohols was not observed on Pt/Al₂O₃. Addition of tin to Pt/Al₂O₃ leads to an important modification of the selectivity since PtSn/Al₂O₃ catalysts produce

an important amount of unsaturated ketones and a small fraction of unsaturated alcohols, this effect being more pronounced at high Sn contents. This behavior appears to be independent of the preparation method. The unsaturated alcohols (mainly carvotanacohol) would be produced from the hydrogenation of carvotanacetone (unsaturated ketone). Then, these unsaturated alcohols are rapidly converted into carvomenthol (saturated alcohol). It must be indicated that PtGe/Al₂O₃ catalysts showed a similar behavior than that of PtSn/Al₂O₃ samples though the production of unsaturated alcohols was lower.

From these results, it can be concluded that the Sn or Ge addition to Pt/Al₂O₃ produces a decrease of the catalytic activity, but the selectivities to the formation of unsaturated ketones and unsaturated alcohols are enhanced. These effects can be related to a modification of the structure of the metallic phase of Pt after adding a second metal like Sn or Ge.

The catalytic behavior in carvone hydrogenation of Pt supported on activated carbon was very different to that of Pt/Al₂O₃ (Figs. 5 and 6). In fact, the Pt/C

Table 2

Selectivity to unsaturated ketones (UK), unsaturated alcohols (UA), saturated ketones (SK) and saturated alcohols (SA) at a carvone conversion = 1 and $T = 313\text{ K}$

Catalyst	M/Pt ^a	Selectivity to (%)			
		UK	UA	SK	SA
Pt/Al ₂ O ₃	–	10	0	90	0
PtSn/Al ₂ O ₃ –SI	0.32	36	0	52	12
PtSn/Al ₂ O ₃ –Co	0.32	9	0	66	25
PtSn/Al ₂ O ₃ –SI	0.49	33	4	54	9
PtSn/Al ₂ O ₃ –Co	0.49	11	2	62	25
PtSn/Al ₂ O ₃ –SI	0.65	35	1	56	8
PtSn/Al ₂ O ₃ –Co	0.65	43	4	36	17
PtGe/Al ₂ O ₃ –SI	0.42	45	0	55	0
PtGe/Al ₂ O ₃ –SI	0.68	58	2	35	5
PtGe/Al ₂ O ₃ –SI	0.99	65	1	32	2
Pt/C	–	96	3	1	0

^a M/Pt: Sn (or Ge)/Pt molar ratio in the catalyst.

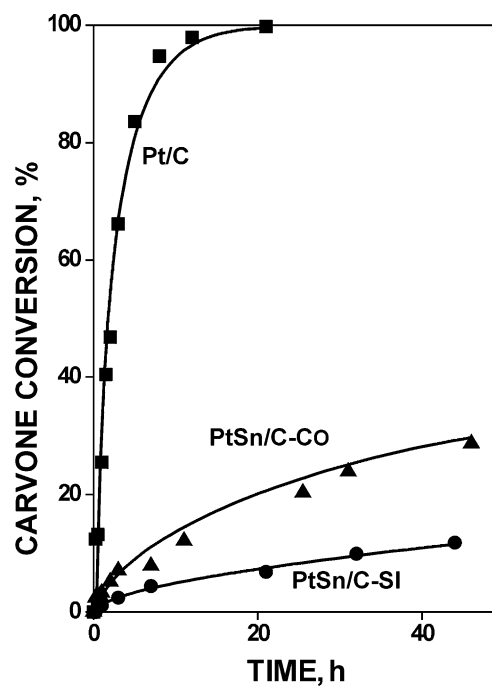


Fig. 5. Carvone conversion as a function of the reaction time for Pt/C and PtSn/C catalysts.

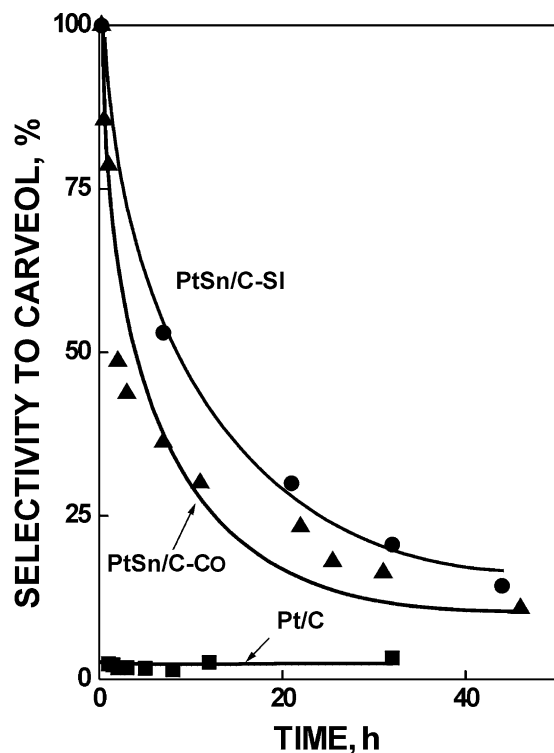


Fig. 6. Selectivity to carveol as a function of the reaction time for Pt/C and PtSn/C catalysts.

sample displays a clear competitive effect between the hydrogenation of the exocyclic $-C=C-$ bond and the $-C=O$ group of the carvone. In this sense, it must be indicated that a small fraction of unsaturated alcohols (composed mainly by carveol) is produced from the initial stages of the reaction and it was maintained along the reaction time. Carveol, the doubly unsaturated alcohol, arises from the direct hydrogenation of carvone, such as Fig. 1 shows.

When Sn is added to Pt/C, a sharp decrease in the catalytic activity is observed, such as Fig. 5 shows. These bimetallic catalysts supported on carbon display a low hydrogenation activity, but they also show a very important modification in the selectivity with respect to the monometallic sample (Fig. 6). In fact, a very high selectivity to carveol (which can reach values close to 100%) is observed at the initial stages of the reaction. For higher reaction times, the selectivity to the doubly unsaturated alcohol decreases up to values close to 15% at the end of the reaction period.

There are important positive effects on the selectivity to unsaturated alcohols both by the support and by the tin addition. The activated carbon as a support for this hydrogenation reaction displays advantages with respect to the alumina since the functional groups of the carbonaceous support would lead to a higher polarization of the $-C=O$ groups of the carvone, thus leading to a direct conversion of carvone into carveol. Likewise, the tin addition to Pt/C appears to produce a strong inhibition of the hydrogenation of $-C=C-$ bonds. This effect can be assigned to the very important surface enrichment of the metallic phase in Sn and to the presence of PtSn alloys. The high surface concentration of Sn blocks free Pt atoms (which decreases the catalytic activity) and the Sn surface ions enhance the polarization of the $-C=O$ group of the carvone, which would be more exposed to be hydrogenated by the hydrogen atoms dissociated in the adjacent sites of Pt.

4. Conclusions

1. Pt/ Al_2O_3 is a very active catalyst for the hydrogenation of carvone, but non-selective since it produces practically only saturated ketones.
2. Tin or Ge addition to Pt/ Al_2O_3 modifies the selectivity similarly, i.e., increasing the selectivity towards unsaturated ketones, and producing very small amounts of unsaturated alcohols, mainly carvotanalphaol.
3. The nature of the support plays an important role both in the activity and in the selectivity. The monometallic Pt/C catalyst, unlike Pt/ Al_2O_3 , is selective since it produces unsaturated ketones and a small fraction of carveol, the doubly unsaturated alcohol. The differences between carbon and alumina as a support could be due to complex reasons, like differences in the metallic dispersions, in the internal distribution of the metallic phase in the catalytic particles, and in the surface chemistry of the support. Besides the bimetallic PtSn/C catalysts display a lower hydrogenation activity than PtSn (or PtGe) supported on alumina, but a very different selectivity, since PtSn/C produce high amounts of unsaturated alcohols (carveol) at the beginning of the reaction.

4. The high selectivity towards unsaturated alcohols in the bimetallic catalysts supported on carbon are due not only to effects of the support but also to a modification of the metallic phase by the tin addition to Pt.
5. The different impregnation sequences used for the preparation of bimetallic catalysts supported both on alumina and on carbon does not produces a substantial modification in the catalytic properties in the carvone hydrogenation reaction.

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