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Catalysis Today 48 (1999) 65–72

CATALYSIS TODAY

Hydrogenation of carvone on Pt–Sn/Al_2O_3 catalysts

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Abstract

The effect of Sn concentration in Pt–Sn/Al_2O_3 catalysts prepared by different procedures on the catalytic behavior in the carvone hydrogenation in liquid phase was studied. Results indicated that the increase of the Sn amount added to Pt modified the catalytic behavior, favoring the formation of unsaturated ketones and the simultaneous production of small quantities of unsaturated alcohols as reaction intermediaries. On the other hand, Pt/Al_2O_3 catalyst only produced carvomenthone as the main reaction intermediary. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Selective hydrogenations; Bimetallic supported catalysts; Fine chemistry

1. Introduction

One of the major problems in synthesis processes for Fine Chemistry is related to the selective reduction of organic molecules with different functional groups [1]. Heterogeneous Catalysis plays an important role in these reactions. The use of solid catalysts displays advantages for the handling and catalyst separation from the reaction medium. Besides, the use of model molecules appears as an adequate way to study selective hydrogenations on solid catalysts. In this sense the carvone molecule (a monocyclic terpenic ketone) is a very interesting case, since the transformation of carvone into more valuable products (such as unsaturated ketones and alcohols) appears to be a good alternative. From a basic point of view, carvone is a very adequate model molecule since it has three functional groups that are capable of being hydrogenated: a –C=O group, an endocyclic –C=C– group and an exocyclic –C=C group. From the point of view of chemical reactivity, the –C=C– bonds appear to have a different behavior than that of the –C=O group.

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 (crotonaldehyde, acrolein, cinnamaldehyde, citral, etc.) has been extensively studied lately [1–5]. However, it should be indicated that 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 [6–8]. Among bimetallic catalysts, supported Pt–Sn ones emerge as a very interesting system. In fact, 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 unsatu-

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PII: S0920-5861(98)00359-9

rated aldehydes and ketones [3,5]. On these bases we carried out an exploration on the behavior of supported Pt–Sn catalysts in the carvone hydrogenation in liquid phase. Thus, Pt–Sn/Al_2O_3 catalysts with different Sn contents were prepared by using different impregnation procedures (successive impregnation and coimpregnation). Furthermore, catalysts were also characterized by using temperature programmed reduction (TPR), H_2 chemisorption and test reactions of the metallic phase (cyclohexane dehydrogenation and cyclopentane hydrogenolysis).

2. Experimental

Two Pt (1 wt%)Sn/Al_2O_3 catalyst series with different Sn contents (0.2, 0.3 and 0.4 wt%) were prepared by using two methods: successive impregnation (SI) and coimpregnation (C). In the first case, a commercial γ-Al_2O_3 (pre-calcined at 923 K) was impregnated with an aqueous solution containing H_2PtCl_6 and HCl (0.4 M), dried at 393 K for 12 h, and then calcined at 773 K during 3 h. Then this precursor was impregnated with hydrochloric acid solution of $SnCl_2$, dried at 393 K overnight, and finally calcined at 773 K. In the case of coimpregnated catalysts, the support was impregnated with a solution containing H_2PtCl_6, $SnCl_2$ and HCl. After impregnation, samples were dried at 393 K overnight and finally calcined at 773 K during 3 h. In all cases of successive impregnation and coimpregnation, the ratio between the volume of the impregnating solution and the weight of the solid was 1.4 cm^3/g, and the concentrations of the metallic precursors in the impregnating solutions were such as to obtain the desired loadings in the catalysts.

Catalysts were evaluated in the carvone hydrogenation reaction at 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 was hydrogenated by using 0.40 g of catalyst and 30 cm^3 of toluene. The influence of the resistances to the mass transport was not very important under these reaction conditions. The hydrogenation experiments were carried out at 313 and 363 K. Reaction products were intermittently withdrawn from the reactor and analyzed in a GC chromatographic system with a capillary column (Supelcowax 10 M). Previous to the reaction, catalysts were reduced in situ with H_2 at 773 K during 3 h, and then they were cooled down to the reaction temperature. Additional experiments on the hydrogenation of carvomenthone under similar conditions were also performed.

Catalysts were characterized by temperature programmed reduction (TPR) using a H_2 (5% v/v)–N_2 mixture and a heating rate of 6 K/min. Test reactions of the metallic phase were carried out in a differential flow reactor at 573 K for cyclohexane (CH) dehydrogenation and at 623 K for cyclopentane (CP) hydrogenolysis. CH dehydrogenation was performed using a H_2/CH molar ratio of 26 and a CH volumetric flow of 6 cm^3/min. Reaction conditions for CP hydrogenolysis were: H_2/CP molar ratio=22.5 and CP volumetric flow=6 cm^3/min. Before reaction, catalysts were reduced with flowing H_2 at 773 K for 3 h. The catalyst weight used in both test reaction experiments was such as to obtain a conversion lower than 5%. The activation energy of the CH dehydrogenation reaction was obtained by measuring the catalytic activity at three temperatures: 543, 558 and 573 K. Hydrogen chemisorption was carried out at room temperature in a volumetric equipment. In these experiments, catalysts were previously reduced at 773 K during 5 h, then outgassed under vacuum (10^{-5} Torr) at the same temperature during 1 h and finally the samples were cooled down to 298 K.

3. Results and discussion

Table 1 shows the initial reaction rates of cyclohexane dehydrogenation (R_{CH}) and cyclopentane hydrogenolysis (R_{CP}) for both catalysts series. Moreover, the activation energy (E_{CH}) in cyclohexane dehydrogenation and the H_2 chemisorption capacities (H) were also included in Table 1. Results show that the Sn addition to Pt produces an important decrease in both reaction rates and in the amount of chemisorbed H_2. Taking into account the insensitive character of the CH dehydrogenation reaction [9], the important increase of the activation energy (E_{CH}) when the Sn amount added to Pt increases, would indicate a modification of the nature of the active metallic sites. Furthermore, the sharp decrease of the CP hydrogenolysis activity (a structure-sensitive reaction [10]) for

Table 1
H_2 chemisorption capacities (H), initial rates (R_{CH}) and activation energies (E_{CH}) in the cyclohexane dehydrogenation, and initial rates in the cyclopentane hydrogenolysis (R_{CP}) for Pt(1 wt%)/Al_2O_3 and Pt(1 wt%)Sn/Al_2O_3 catalysts with different Sn contents, prepared by successive impregnation (Pt–Sn-SI) and coimpregnation (Pt–Sn-C)

Sample	Sn content (wt%)	H (μmol/g)	R_{CH} (mol/h g Pt)	E_{CH} (kcal/mol)	R_{CP} (mol/h g Pt)
Pt/Al_2O_3	0.0	27.6	52.3	19±1	13.0
Pt–Sn-SI	0.2	18.2	29.8	24±1	0.6
Pt–Sn-SI	0.3	8.8	21.9	30±1.5	0.18
Pt–Sn-SI	0.4	3.9	11.7	29±1.5	0.11
Pt–Sn-C	0.2	15.6	29.6	21±1	1.11
Pt–Sn-C	0.3	8.6	23.6	22±1	0.16
Pt–Sn-C	0.4	3.4	12.1	30±1.5	0.06

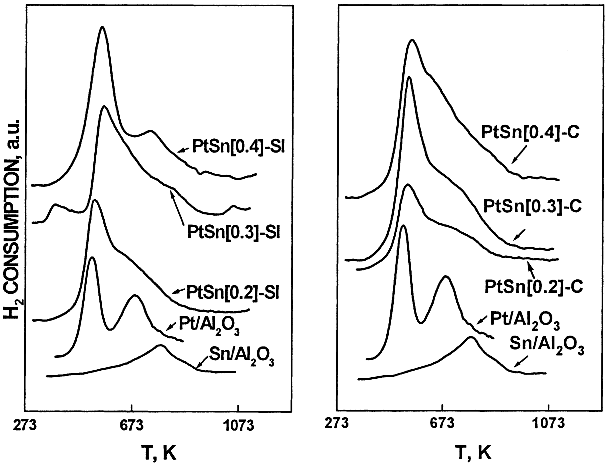

Fig. 1. TPR profiles of Pt/Al_2O_3, Sn/Al_2O_3 and Pt–Sn/Al_2O_3 catalysts prepared by successive impregnation (Pt–Sn-SI), and coimpregnation (Pt–Sn-C). The number between brackets indicates the Sn content.

catalysts with increasing amounts of Sn could be related to an electronic change of Pt by the Sn addition, as several authors reported [11–16]. Other evidences on the Pt–Sn interaction were observed from TPR results (Fig. 1). In fact, bimetallic samples show an important reduction zone at about 523 K, temperature corresponding to the Pt reduction in Pt/Al_2O_3 catalysts. This fact and the negligible reduction zone at high temperatures (>700 K), where Sn (in Sn/Al_2O_3) is reduced, would indicate a co-reduction of both metals with probable alloys formation. It must also be noted that both catalysts series display similar TPR profiles, though the broadening of the main reduction peak and the presence of a small shoulder at 690 K in SI catalysts (with respect to C catalysts) would indicate a stronger interaction in the coimpregnated catalyst series. The presence of this shoulder at about 690 K would be related to the existence of a small fraction of free Sn particles separated from Pt ones. However, the differences between TPR profiles of both catalysts series are not very important.

Fig. 2 shows the relative activity in the carvone hydrogenation as a function of the Sn content for both catalyst series and for different reaction temperatures. The relative activity was defined as the ratio between the time required for the total disappearance of carvone for Pt/Al_2O_3 at 313 K $(\Theta^*_{\mathrm{Pt},313\,\mathrm{K}})$ and that corresponding to a given bimetallic catalyst at different reaction temperatures $(\Theta^*_{\mathrm{Pt-Sn},T})$. Results show that when the Sn amount added to Pt increases, the relative

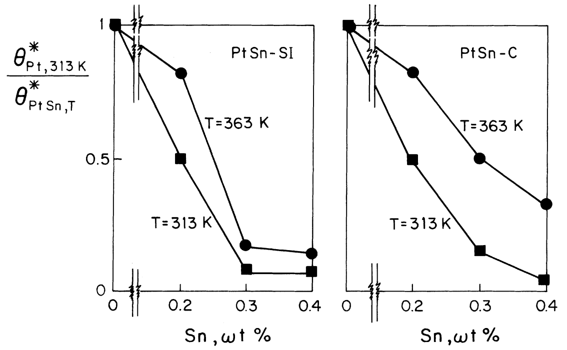

Fig. 2. Relative activity $(\Theta^*_{\mathrm{Pt},313\,\mathrm{K}}/\Theta^*_{\mathrm{Pt-Sn},T})$ in carvone hydrogenation versus Sn content for different catalysts (Pt–Sn-SI: successively impregnated catalysts, Pt–Sn-C: coimpregnated samples) and reaction temperatures. $\Theta^*_{\mathrm{Pt},313\,\mathrm{K}}$: time required for the total disappearance of carvone for Pt/Al_2O_3 at 313 K; $\Theta^*_{\mathrm{Pt-Sn},T}$: time required for the total disappearance of carvone for $Pt–Sn/Al_2O_3$ at a given reaction temperature (T).

activity decreases for both bimetallic catalysts series. Moreover, the relative activity also increases with the reaction temperature for a catalyst with a given Sn content, this effect being more pronounced for coimpregnated samples.

The carvone hydrogenation reaction was divided into two stages for the analysis of the distribution of the reaction products. The first stage corresponds to the evolution of the reaction until carvone was completely depleted from the reaction medium. The second stage corresponds to the interconversion of the different compounds obtained during the first stage. Fig. 3(a) and Fig. 4(a) show the evolution of the different reaction products during the first reaction stage as a function of the carvone conversion for SI catalysts series at 313 and 363 K, respectively. For the Pt/Al_2O_3 catalyst, it can be observed that carvomenthone is the major product at both reaction temperatures, and that a low concentration of unsaturated ketones (selectivity to carvotanacetone $\cong$10%) is produced. When the Sn concentration on the catalysts increases, increasing amounts of unsaturated ketones (carvotanacetone and dihydrocarvone) are initially produced from carvone. As the reaction progresses, the unsaturated ketones are progressively transformed first into carvomenthone and then into carvomenthol. By analyzing the sequence of the reaction products along the first reaction stage, it can be observed that carvomenthol would be mainly produced from the hydrogenation of carvomenthone. For catalysts with higher Sn contents (0.3 and 0.4 wt%), small amounts of unsaturated alcohols (carvotanalcohol) were produced at low carvone conversions. A similar behavior was found for the C-series.

Fig. 5 compiles the yield values to different products (measured at the carvone conversion equal to 1) for different catalysts and reaction temperatures. It is observed that the Sn addition to Pt produces a very important modification in the selectivity. In fact, when the Sn amount added to Pt increases, the yield to unsaturated ketones increases and that to carvomenthone decreases, these effects being more pronounced for higher Sn contents in both catalysts series. The yield to carvomenthol displays a maximum at a Sn content=0.2 wt%, which appears to be more pronounced when the reaction temperature increases from 313 to 363 K. It must be noted that low amounts of unsaturated alcohols were detected only in samples with high Sn concentrations (except for Pt–Sn–C catalyst evaluated at 363 K).

Among the unsaturated ketones, dihydrocarvone and carvotanacetone were detected as intermediaries during the first reaction stage. It was also observed that these unsaturated ketones were simultaneously produced at low carvone conversion, but carvotanacetone was always the main product at high conversion. Fig. 6 compiles the DH/(DH+CA) molar ratio values (DH: dihydrocarvone, CA: carvotanacetone) at carvone conversion=1 for different catalysts and reaction temperatures. It can be noted that the dihydrocarvone remained in the reaction medium (at carvone conversion=1) for catalysts with an Sn content of 0.4 wt% at 313 K and for samples with an Sn content $\geq$0.3 wt% at 363 K. In all cases the DH/(DH+CA) molar ratio increases with the Sn content and with the reaction temperature, reaching a value close to 25% for Pt–Sn(0.4)-C at 363 K. The higher selectivity of Pt–Sn catalysts to unsaturated ketones with respect to that of the Pt/Al_2O_3 catalyst could be related to structural modifications of the metallic phase by the Sn addition, which would lead to changes in the catalytic properties. Results clearly show that Pt/Al_2O_3 is a non-selective catalyst, since both the endo and exocyclic –C=C– bonds of carvone are rapidly hydrogenated to carvomenthone. The addition of increasing amounts of Sn to Pt not only decreases the overall hydrogenation rate but also leads to a competitive hydrogenation

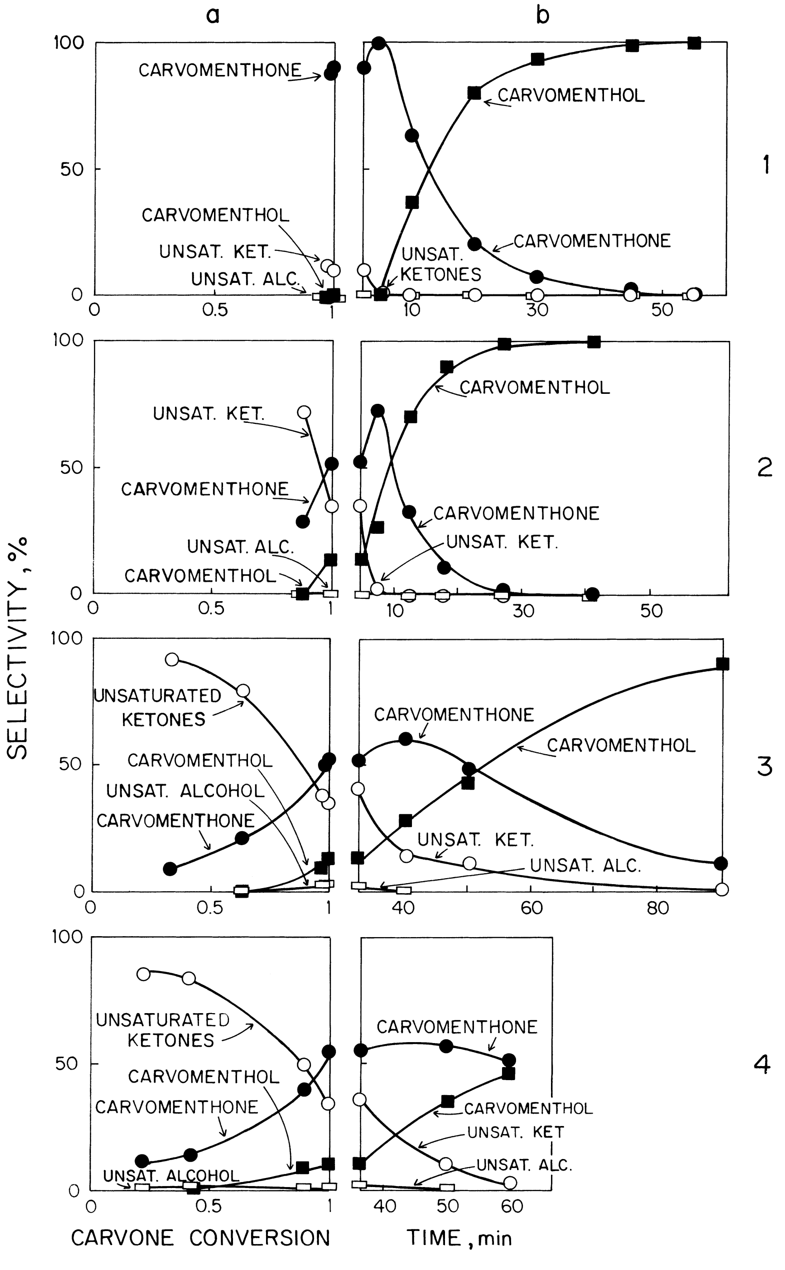

Fig. 3. Distribution of products for Pt–Sn/Al_2O_3 samples prepared by successive impregnation (SI). (a) and (b): first and second reaction stages, respectively. *T*: 313 K. (1) Pt (1 wt%)/Al_2O_3; (2) Pt–Sn (0.2 wt%)/Al_2O_3; (3) Pt–Sn (0.3 wt%)/Al_2O_3; (4) Pt–Sn (0.4 wt%)/Al_2O_3.

between the exocyclic and endocyclic –C=C– bonds, such as is evidenced by the simultaneous formation of carvotanacetone and dihydrocarvone at the beginning of the reaction. However, the hydrogenation of the exocyclic double bond appears to be faster than the endocyclic one, such as the values of the DH/(DH+CA) molar ratio reveals.

The formation of low amounts of unsaturated alcohols at the beginning of the reaction on bimetallic catalysts with high Sn contents would indicate

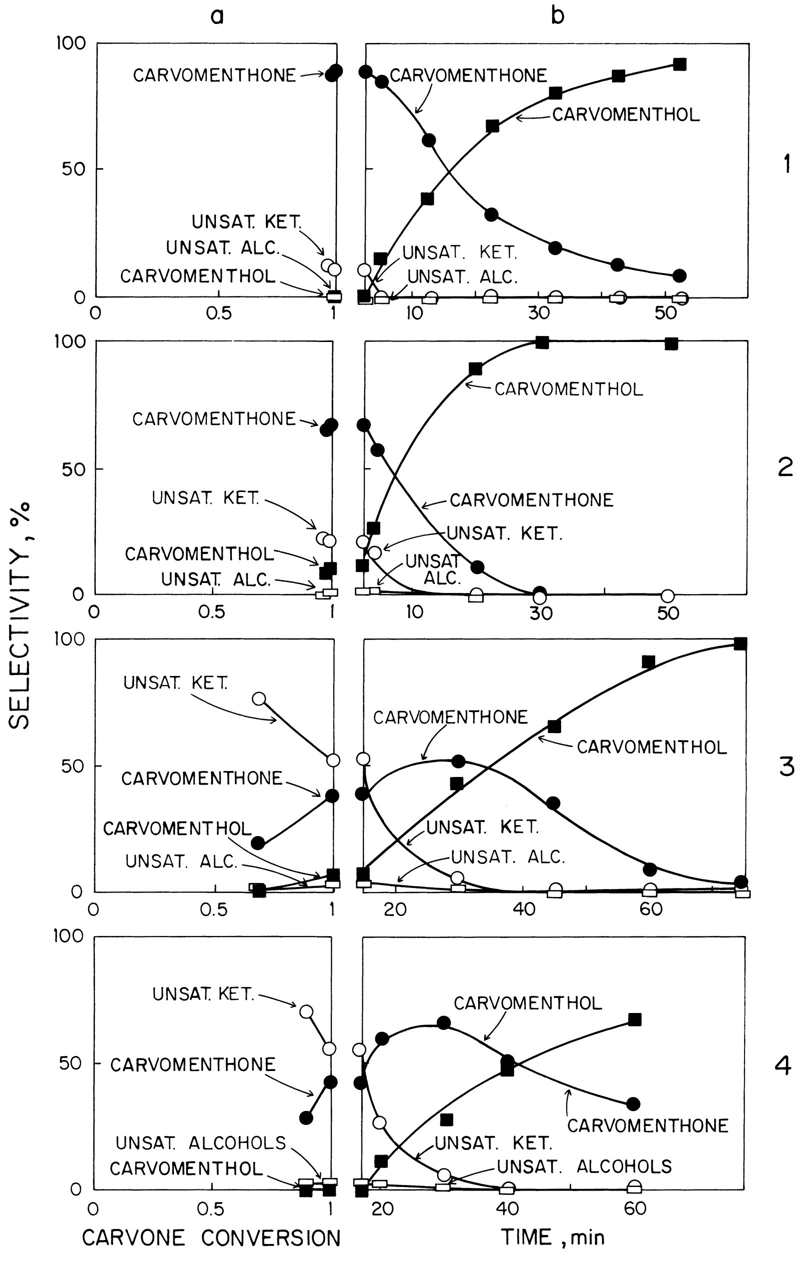

Fig. 4. Distribution of products for Pt–Sn/Al_2O_3 samples prepared by successive impregnation (SI). (a) and (b): first and second reaction stages, respectively. *T*: 363 K. (1) Pt (1 wt%)/Al_2O_3; (2) Pt–Sn (0.2 wt%)/Al_2O_3; (3) Pt–Sn (0.3 wt%)/Al_2O_3; (4) Pt–Sn (0.4 wt%)/Al_2O_3.

a small competitive effect between the hydrogenation of –C=C– bonds and that of the –C=O group. It must be noted that unsaturated alcohols involved carvotanalcohol as the main product and small quantities of dihydrocarveol. No formation of carveol (through the selective hydrogenation of the –C=O bond of carvone) was found for these catalysts and under these experimental conditions. Hence, carvotanalcohol and dihydrocarveol would be obtained exclusively from the

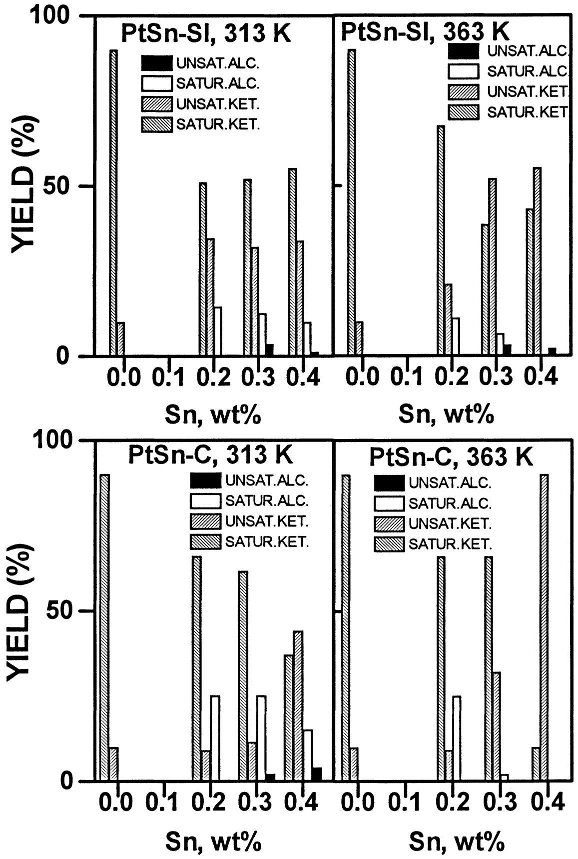

Fig. 5. Yield to different reaction products at carvone conversion=1 for Pt–Sn/Al_2O_3 catalysts prepared by successive impregnation (Pt–Sn-SI) and coimpregnation (Pt–Sn-C) as a function of the Sn content and for different reaction temperatures (313 and 363 K).

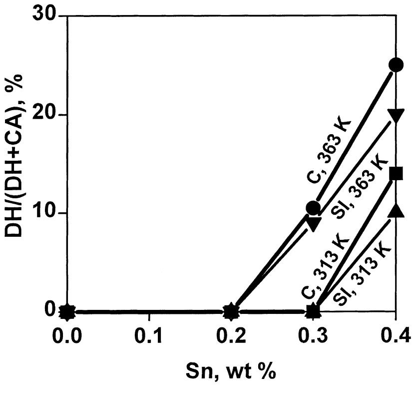

Fig. 6. DH/(DH+CA) molar ratio values for different Pt–Sn/Al_2O_3 catalysts prepared by successive impregnation (SI) and coimpregnation (C), as a function of the Sn content and for different reaction temperatures. DH: dihydrocarvone, CA: carvotanacetone.

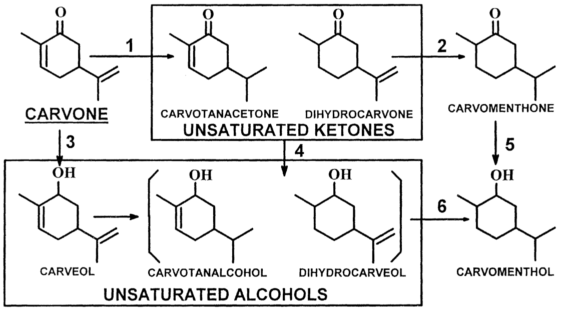

Fig. 7. Reaction scheme of carvone hydrogenation.

hydrogenation of carvotanacetone and dihydrocarvone, respectively.

Taking into account the above-mentioned results, the transformation of carvone into intermediary and final products can be described by the reaction scheme shown in Fig. 7.

According to the results shown in Figs. 3 and 4, it can be concluded that the rates of steps 1 and 2 (reaction scheme, Fig. 7) are very fast for the Pt/Al_2O_3 catalyst. When increasing amounts of Sn are added to Pt, the transformation rate of unsaturated ketones into carvomenthone (step 2, Fig. 7) decreases with respect to the reaction rate of step 1. The formation of unsaturated alcohols could take place from carvone (step 3) or by hydrogenation of unsaturated ketones (step 4). Since no carveol formation was detected in any case, the second route (hydrogenation of ketones, step 4) would be the major path for the production of unsaturated alcohols on Pt–Sn/Al_2O_3 catalysts with high Sn contents. Carvomenthone and unsaturated alcohols are transformed into the saturated alcohol (carvomenthol) through steps 5 and 6. Furthermore, results of additional experiments on carvomenthone hydrogenation showed that there was an optimum concentration of Sn (0.2 wt%) in the bimetallic catalyst which maximized the production of carvomenthol from carvomenthone. This optimum for the carvomenthol production was also observed in the carvone hydrogenation at the end of the first reaction stage, such as Fig. 5 shows.

Fig. 3(b) and Fig. 4(b) display the evolution of the different reaction products along the time during the second reaction stage. It is observed that unsaturated ketones are progressively transformed into carvomenthone, which is then converted into carvomenthol at the end of the reaction. For bimetallic catalysts with Sn amount >0.2 wt%, both the transformation rate of unsaturated ketones into carvomenthone and the carvomenthol formation are slower than those corresponding to the monometallic catalyst. Furthermore, it can be observed that the unsaturated alcohols progressively disappear from the reaction medium at the beginning of this second reaction stage.

4. Conclusions

The Sn addition to Pt modifies the selectivity in the carvone hydrogenation reaction. In this sense, results presented in this paper indicate that Pt–Sn/Al_2O_3 system shows a good selectivity to unsaturated ketones, mainly at 363 K and for high Sn contents (conditions in which a selectivity value to unsaturated ketones close to 90% is obtained). Similar results were found for Rh supported catalysts [7] and for Pt–Au/SiO_2 [8]. However, several differences among these catalytic systems must be pointed out. Both the formation of dihydrocarvone and the production of small amounts of unsaturated alcohols (at carvone conversion=1) were found only for Pt–Sn/Al_2O_3 catalysts but not for Rh and Pt–Au supported catalysts [7,8]. With respect to the formation of unsaturated alcohols, it must be indicated that the selective activation of the C=O group of the carvone molecule to produce these unsaturated alcohols by Pt–Sn/Al_2O_3 catalysts was clearly lower than that of other α,β unsaturated aldehydes and ketones, such as cinnamaldehyde, acrolein, crotonoaldehyde, citral, etc. [1–5] for the same catalytic system. Furthermore, it can be also concluded that the use of different impregnation methods (successive impregnation and coimpregnation) does not lead to a different catalytic behavior in this reaction.

Acknowledgements

This project is part of JICA (Japan International Cooperation Agency)–CENACA (Centro Nacional de Catálisis – Argentina) Program. This work was carried out with the financial support of the Secretary of Science and Technology (Universidad Nacional del Litoral, Argentina), CAI+D Program.

References

[1] P. Fouilloux, Heterogeneous Catalysis and Fine Chemicals I, 1988, Elsevier, Amsterdam, p. 123.
[2] V. Ponec, Appl. Catal. A 149 (1997) 27.
[3] F. Coloma, A. Sepúlveda-Escribano, J.L.G. Fierro, F. Rodríguez-Reinoso, Appl. Catal. A 148 (1996) 63.
[4] K. Yoshikawa, Y. Iwasawa, J. Molec. Catal. A 100 (1995) 115.
[5] G. Neri, S. Milone, A. Donato, L. Mercadante, A.M. Visco, J. Chem. Tech. Biotechnol. 60 (1994) 83.
[6] R. Melendrez, G. del Angel, P. Marecot, J. Barbier, Proceedings of the XIII Iberoamerican Symposium on Catalysis, vol. I, Segovia, Spain, 1992, p. 183.
[7] R. Gómez, J. Arredondo, N. Rosas, G. del Angel, Heterogeneous Catalysis and Fine Chemicals II, Elsevier, Amsterdam, 1991, p. 185.
[8] G. del Angel, R. Melendrez, V. Bertin, J.M. Domínguez, P. Marecot, J. Barbier, Heterogeneous Catalysis and Fine Chemicals III, Elsevier, Amsterdam, 1993, p. 171.
[9] D.N. Blakely, G.A. Somorjai, J. Catal. 42 (1976) 181.
[10] C.R. Apesteguía, J. Barbier, Proceedings of the Eighth Iberoamerican Symposium on Catalysis, Huelva, Spain, 1982, vol. II, p. 751.
[11] V.H. Berndt, H. Mehner, J. Volter, W. Meisel, Z. Anorg. Allg. Chem. 429 (1977) 47.
[12] R. Srinivasan, R.J. De Angelis, B.H. Davis, J. Catal. 106 (1987) 449.
[13] R. Bacaud, P. Bussiere, F. Figueras, J. Catal. 69 (1981) 399.
[14] V.I. Kuztnesov, A.S. Belyi, E.N. Yurchenko, M.D. Smolikov, M.T. Protasova, E.V. Zatolokina, V.K. Duplyakin, J. Catal. 99 (1986) 159.
[15] S.R. de Miguel, G.T. Baronetti, A.A. Castro, O.A. Scelza, Appl. Catal. 45 (1988) 61.
[16] S.R. de Miguel, A.A. Castro, O.A. Scelza, J.L.G. Fierro, J. Soria, Catal. Lett. 36 (1996) 201.