SELECTIVE HYDROGENATION OF CITRAL ON Pt-Sn/SiO_2: EFFECT OF THE TEMPERATURE OF CALCINATION

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The selective hydrogenation of the citral for production of unsaturated alcohol (geraniol and nerol) was considered a complex process of three phases: gaseous, liquid and solid. The catalysts used in reaction were Pt-Sn/SiO_2 with metallic contents of 4.2%Pt e 0.8%Sn, prepared by co-impregnation with precursors: $H_2PtCl_6.14H_2O$ and $SnCl_2.4H_2O$. The catalysts impregnated were submitted to the thermal treatment of drying, calcination and reduction and characterized by different techniques to determine its physics and chemicals properties. In this work is proposed to discuss the effect of temperature of calcination on catalysts Pt-Sn/SiO_2 in selective hydrogenation of citral to produce unsaturated alcohol. The catalysts Pt-Sn/SiO_2 calcinated in different temperatures were submitted to the reaction and after 2 hours of reaction show a high activity, a complete conversion and increase selectivity up to 79%. The results were associated to the particle size of the metallic phase (Pt) obtained by effect of thermal treatment and superficial segregation of tin and platinum.

Key words: hydrogenation, citral, Pt-Sn, calcination temperature.

1. Introduction

The alcohol α,β-unsaturated are products of difficult access and expensive. For example the geraniol is extracted of palmarosa (70-85%) (Kurt et al., 1985) and lemon oil (75-85%) (Poucher, 1991) and others are prepared by direct and indirect selective hydrogenation of aldehyde α,β-unsaturated. Chemical reducer, e.g. isopropilato of aluminum and metallic hydrates (reaction of MEERWEIN-PONDORF-VERLEY), makes the indirect selective hydrogenation. These chemical reagents are very expensive and difficultly recycle.

The direct selective hydrogenation with heterogeneous catalysis is considered a more alternative economic. This selectivity depends of the addition of hydrogen to a certain position of the conjugated system to hydrogenate the function carbonyl without reacting with other functions of the citral as shown in Figure 1. The selectivity can be processed to the alcohol unsaturated, aldehyde unsaturated and enol, which can isomer to saturated aldehyde, also the hydrogenation can continue to produce the saturated alcohol and hydrocarbon. Furthermore the hydrocarbon can be produced by the hydrogenolise of C-O, but it is not very frequent. In reference to the hydrogenation of the citral to unsaturated alcohol was found that the selectivity was improved with the addition of Sn to Rh or Ru on silica (by means of organometallic) (Didillon et al., 1991), in catalysts Rh-Sn/SiO_2 was improved the activity and the selectivity to unsaturated alcohol near 95% (by means of co-impregnation) (Nishiyama et al., 1997; Lobão et al., 1998).

The citral is a polyfunctional molecule, a family member of the aldehydes α,β-unsaturated of two isomeric citral a (cis, geranial) and citral b (trans, neral). The citral has three unsaturations: an aldehyde function (group carbonyl), a conjugated couple (conjugated olefin) and an isolated couple (isolated olefin). This characteristic turns very difficult the syntheses of the complex molecule of citral, due to the high range of products from the simple and multiple reactions as shown in Figure 1, and complex stage of separation of the obtained products.

The catalysts used in reaction were Pt-Sn/SiO_2 with metallic contents of 4.2%Pt e 0.8%Sn, prepared by co-impregnation with precursors: $H_2PtCl_6.14H_2O$ and $SnCl_2.4H_2O$. The catalysts impregnated were submitted to the thermal treatment of drying, calcination and reduction and characterised by different techniques such as the Atomic absorption, Scanning Electronic Microscopy, Difraction of Ray-X, Temperature Programmed Reduction, Termogravimetry Analysis and Chemisorption to determine its physic and chemical properties.

The main difficult in the hydrogenation of aldehyde α,β-unsaturated is the electronics effects due to the conjugated couple of the functions C=C and C-O separately. Under moderate reaction conditions in presence of (Pd, Pt and Ni) the couple ethylenics is more easily hydrogenated than the couple carbonyl. Bearing this in mind in this work is proposed to discuss the effect of temperature of calcination on catalysts Pt-Sn/SiO_2 in selective hydrogenation of the citral to produce unsaturated alcohol of geraniol and nerol, also to evaluate the effect of thermal treatment of calcination and reduction temperatures. The catalysts Pt-Sn/SiO_2 were calcinated in different temperatures, after 2 hours of reaction showed a high activity, a complete conversion and increase selectivity up to 79% to geraniol and nerol. The results were associated to the particle size of the metallic phase (Pt) and superficial segregation of Sn and Pt that were resulted of the thermal treatment effect.

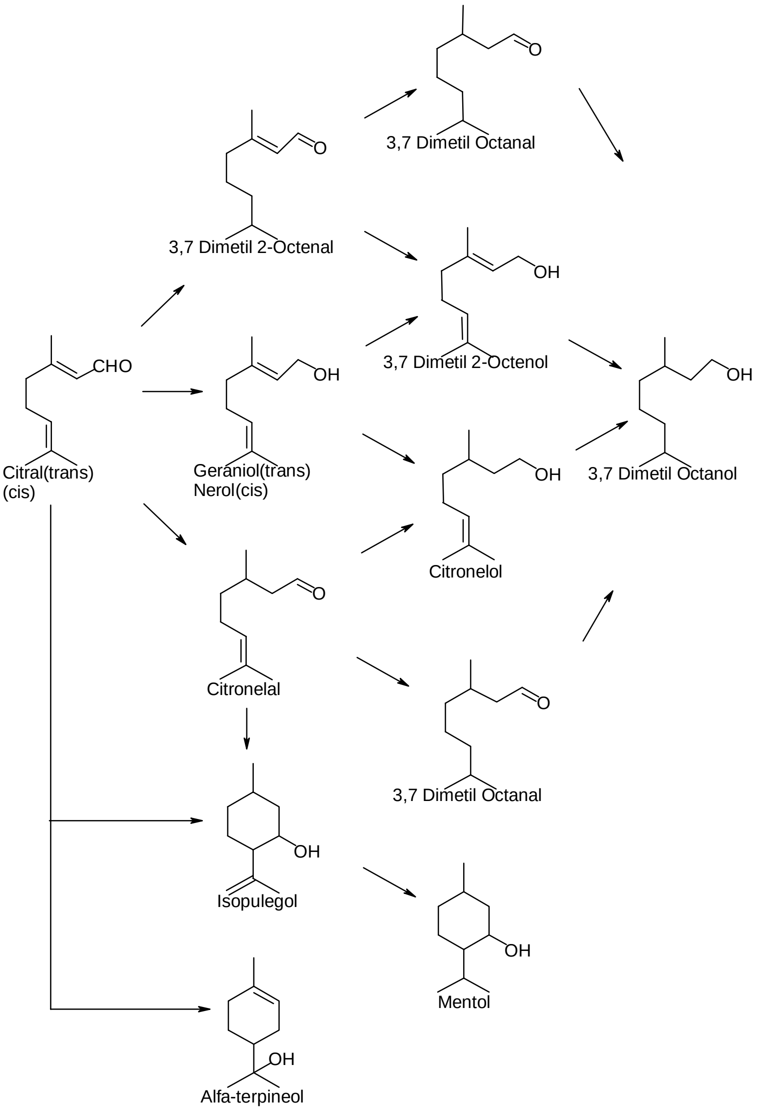


Figure 1 Scheme of the selective hydrogenation of the citral.

2. Methodology

2.1 Materials

The materials like precursor metal were the tin chloride (II), $SnCl_2.4H_2O$ (supplied by Reagen, >98% of purity) and the Acid Hexachloroplatinic, $H_2PtCl_6.14H_2O$ (supplied by Sigma, 98% of purity). The organic solvents were the benzene (supplied by Merck, >95% of purity), Ethanol (supplied by Merck, >95% of purity) and the support was the gel silica, degree 62, mesh 170-250 (supplied by Aldrich). They were used to prepare the catalyst of $Pt-Sn/SiO_2$ (Silva, 1995).

2.2 Treatment of Supports

In order to eliminate the surface impurities like Na and Ca of the gel silica supports were submitted to treatment of drying at 145°C during 48 hours, it washed with 10 mL HNO_3 / g SiO_2 at 100°C, 24 hours with reflux and without agitation, after it were submitted with reflux and agitation at 100°C, 24 hours. Afterwards it were cooled and washed with agitation at 1 hour and without agitation at 12 hours to dilute the nitric acid concentration. The gel silica were separated by filtration and washed with deionized water to get PH=7, dried at 110°C, 24 hours, and calcinated at 300°C, 3 hours. The supports were characterized whit average grain at 0.0075 mm, and pore specific volume at 1.1 cm^3/g determined by Humid Point Method.

2.3 Preparation of the catalysts

The catalysts Pt-Sn/SiO_2 with surface area of 200m^2/g were prepared by means of co-impregnation with the metal contents of 4.2%Pt and 0.8% Sn p/p (molar reason Sn/Pt = 0.3129). The silica support for preparation was used at 10 g, with superficial area of 213 m^2/g and pore volume at 1.1 cm^3/g. The mixture of benzene-ethanol for preparation were used in proportion of 4:1 (Coupé, 1999). The experimental system experimental was a route-evaporator and extractor. With respect to benzene and ethanol were added at 100 mL to the balloon of 1000 cm^3. This balloon was maintained in slow rotation for 15 min, after the precursor metals were dissolved in the balloon with 1.5003 g of acid hexachloroplatinum and 0.1856 g of tin (II), and furthermore 10g of silica. All components in the balloon were kept in constant rotation during 15 hours at room temperature. Finally the solvent excess was eliminated by evaporation in vacuum pressure at 60°C and the impregnated precursors were removed of the balloon and submitted to thermal treatment.

2.4 Thermal Treatment of the catalyst

The catalysts Pt-Sn/SiO_2 were submitted to the thermal treatment of drying to 120°C/15h, calcination to 300 and 500°C/3h and reduced to 150, 200 and 300°C/6h. The air and hydrogen flows were used at 40 ml/min with heating ratio of 10°C/min for the thermal treatment of all catalysts Pt-Sn/SiO_2. After calcination or reduction the catalysts were cooled to room temperature in each case. Immediately after reduction the hydrogen flow was substituted by nitrogen (N_2) flow, it was used like inert gas flow to avoid oxidation of the catalysts. The activation “in situ” was applied to all catalysts before of to add to the reactor, the catalysts and other components were added to the reactor for selective hydrogenation of the citral.

2.5 Reactional System

The Citral, 3,7 dimetil-2, 6-octadienal (97% of purity, with isomeric such like cis, 61% and trans, 36%) at 3.2156 g, tetradecane (99% of purity) at 0.3249g and n-heptane (>99% of purity) were used as reactional mixture (supplied by SIGMA CHEMICAL CO). The n-heptano was used to complete with 20 ml the mixture of the citral and tetradecano in reactant bulb (FR) as shown in Figure 2. The hydrogen was used as reactional gas (supplied by White Martins, 100% of purity). The catalysts mass was used at 300 mg and n-heptano to complete to 60 ml the mixture in the reactor. The stirred tank reactor was used with 300 ml of capacity, and the operational conditions were 50 bar, 126°C, 1500 rpm and volume of the reactional system 80 mL as shown in Figure 2. The reactional products were analyzed with gas chromatographic (Hewlett Packard 5890 series II) (Lobão, 1999). All results of the selective hydrogenation of the citral are shown in the Figures 3 (a)-(k). They exhibit the variation of the composition (%) versus reaction time (h) for 6 hours of reaction.

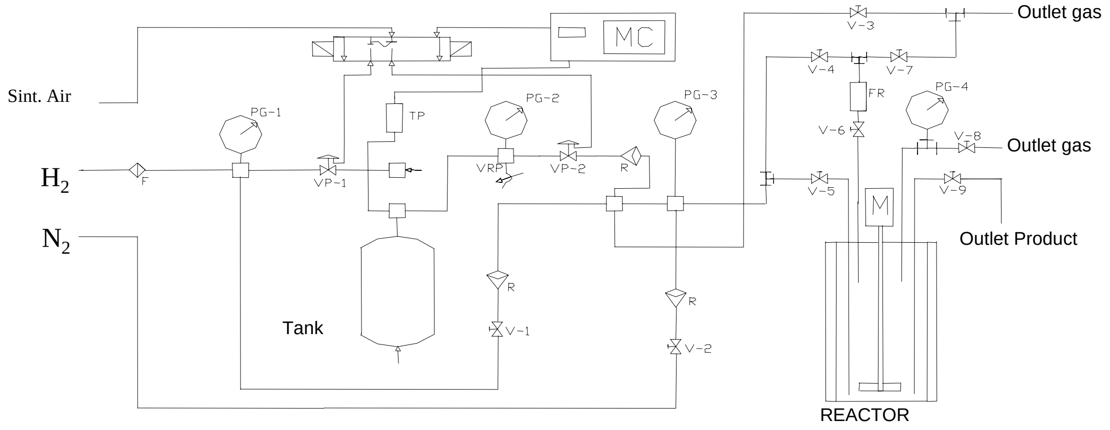
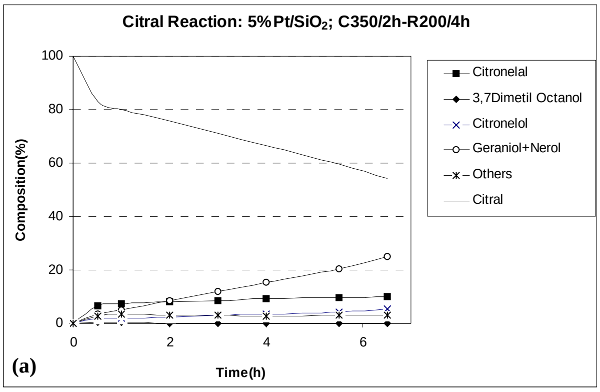
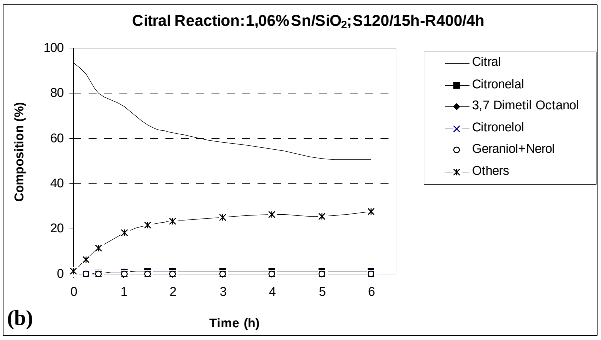


Figure 2 Schematic representation of the reactional system for selective hydrogenation of the citral.

Legend:
PG-1: pressure meter of line,
PG-2: pressure meter of the tank;
PG-3: feed meter of the reactor,
PG-4: pressure meter of the reactor;
V-1, V-2, V-3: valve-needle of the feed module;
V-4, V-5, V-6, V-7, V-8, V-9: operational reactor valve;
M= motor for reactant agitation.
FR= reactant bulb,
VRP= pressure regulator valve;
VP-1 e VP-2= pneumatic valve,
MC= module of control;
TP= transducer of pressure,
F= filter of gas,


Citral Reaction: 5%Pt/SiO$_2$; C350/2h-R200/4h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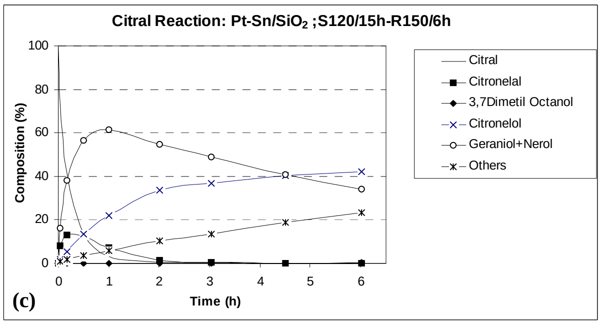
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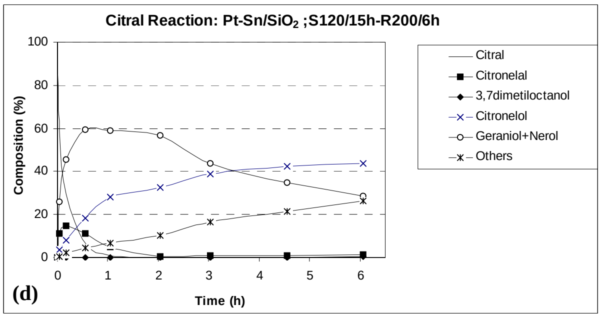
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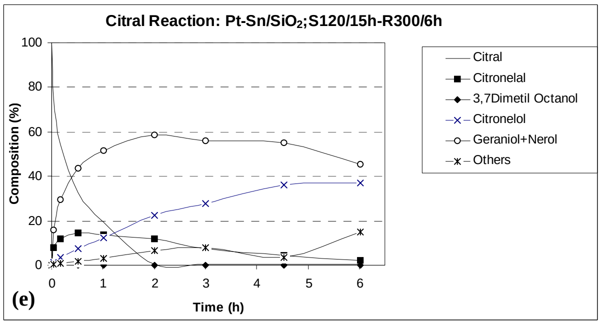
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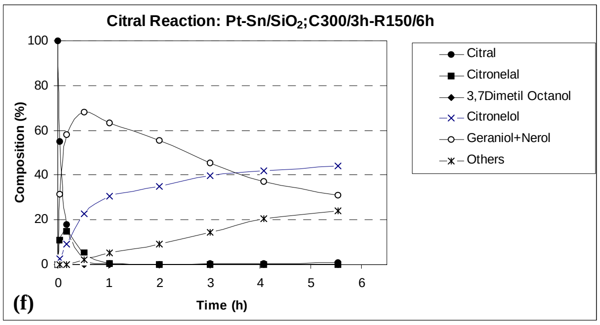
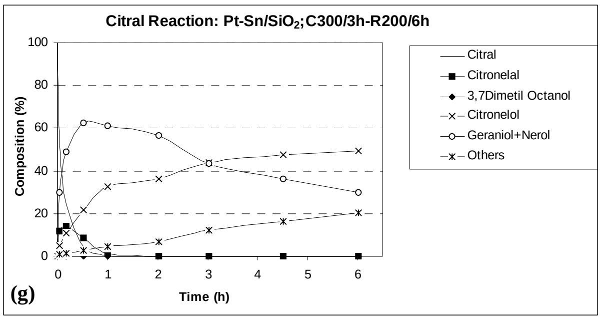
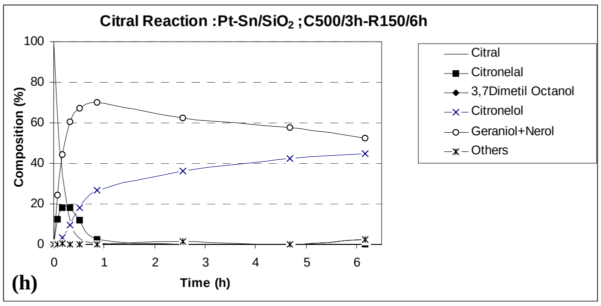

Citral Reaction: Pt-Sn/SiO$_2$;C300/3h-R150/6h


Citral Reaction: Pt-Sn/SiO$_2$;C300/3h-R200/6h


Citral Reaction :Pt-Sn/SiO$_2$;C500/3h-R150/6h

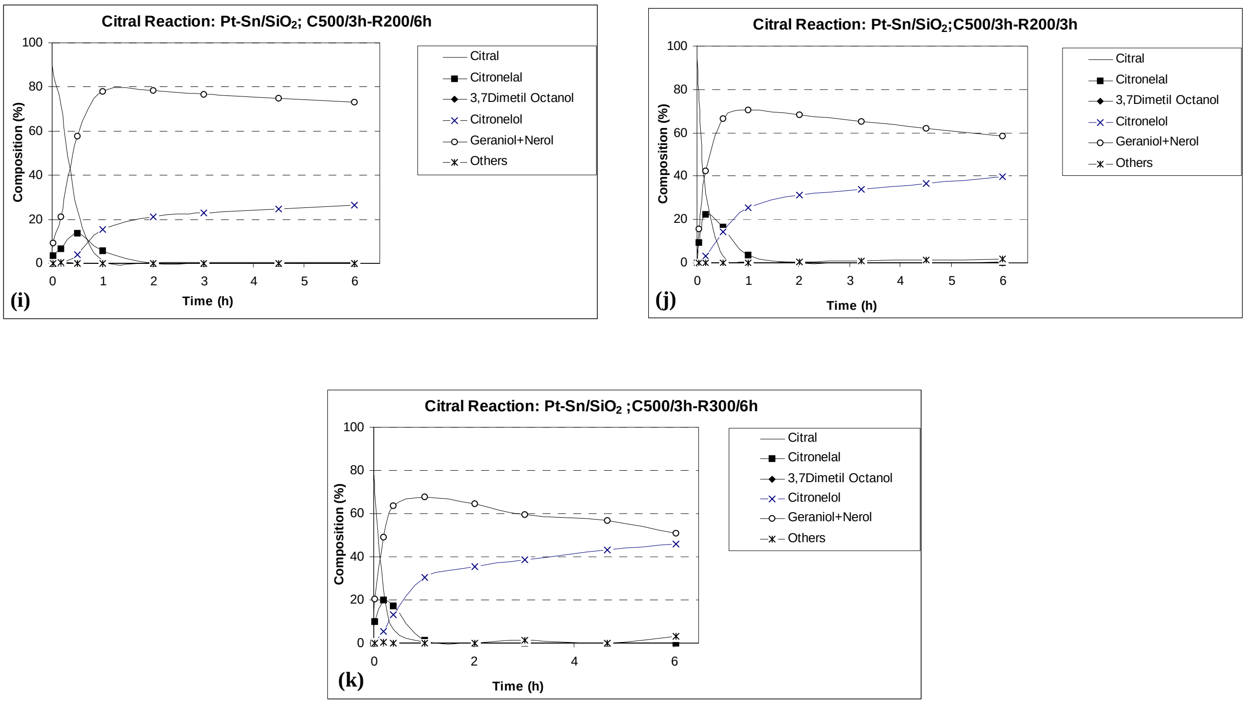


Figure 3 Variation of the composition (%) with reaction time (h) for all monometallic catalysts Pt/SiO_2 and Sn/SiO_2 and bimetallic catalysts Pt-Sn/SiO_2 in the selective hydrogenation of the citral.

3. Results and Discussion

3.1 Effect of the treatment and preparation of the catalysts

According to the treatment of supports were obtained grains of Pt-Sn/SiO_2 smaller than 0.075mm. In relation to the catalyst preparation were obtained high catalytic activity, conversion at 100% and selectivity up to 79% to the allyl alcohols (geraniol and nerol) as shown in Table 1, in case of the bimetallic catalysts. The support treatment procedure and catalysts preparation were evaluated with the Technique of Scanning Electronic Microscopy (SEM), it was observed grain dispersion, agglomeration, and sintering of metal particles, also it was measured the metal particle size. The behavior of the reaction system was analyzed in variable calcination and constant reduction temperature.

The selective hydrogenations of the citral were analyzed in this work for two hours of reaction for all catalysts as shown in Table 1. These results exhibit in “OTHERS” different products like 2,6-Dimetil-octane, 2,6 Dimetil-2-Octeno, Cis-2, 6-Dimetil-2, 6-Octeno, Trans-2, 6-Dimetil-2, 6-Octadieno, 1-Limoneno, α-Terpineol (β,γ,δ), 3,7 Dimetil 2-Octenal, 3,7 Dimetil Octanal (Dihidrocitronelal), Isopulegol (neo-isopulegol, iso-isopulegol, neoiso-isopulegol) and Menthol (neomentol, isomentol, neoisomentol) that were identified by Spectroscopy of Mass. The temperature effects were evaluated with mass reaction speed and citral conversion for activity and selectivity for the allyl alcohols of geraniol and nerol. The monometallic catalysts were also analyzed to compare the effects of Pt and Sn supported in gel silica like exhibit in Table 1.

3.2 Effect of the metal Pt and Sn

The catalysts Pt/SiO_2 showed a low conversion and selectivity to geraniol and nerol (Figure 3 (a) and Table 1), but the catalysts Sn/SiO_2 showed high catalytic activity and null selectivity to the desired products (Figure 3 (b) and Table 1). The scheme I and II (Figure 4) are resulted of the selective hydrogenation of the citral as shown in Figures 3 (a) and (b) respectively, it allowed to describe the way of the reaction of the monometallic catalysts. Now the Termogravimetry Analysis (TGA) allowed to understand the low conversion, null and low selectivity obtained by effect of the thermal treatment. With TGA were determined the lost mass after preparation, calcination and reduction of the catalysts. The lost mass can be by the presence of humidity, chlorine like chlorine compound, reaction products which can be volatile, unstable, to suffer decomposition, oxidation, reduction or to generate complex compound or to break the physical or chemical linkages.

Table 1 Results of the Selective Hydrogenation of the Citral for 2 hours of Reaction.

Catalyst	Thermal Treatment	r_P*10^2 (mmol/g.h)	X_A (%)	Selectivity(%)				
				G+N	CAL	3,7OL	COL	OTHERS
%5Pt/SiO_2	C350/2h-R200/4h	9	15	8	8	-	3	81
1,06%Sn/SiO_2	S120/15h-R400/4h	829	37	-	5	-	-	95
Pt-Sn/SiO_2	S120/15h-R150/6h	403	100	55	1	-	34	10
Pt-Sn/SiO_2	S120/15h-R200/6h	862	100	57	0	-	33	10
Pt-Sn/SiO_2	S120/15h-R300/6h	409	100	59	12	-	23	6
Pt-Sn/SiO_2	C300/3h-R150/6h	728	100	56	-	-	35	9
Pt-Sn/SiO_2	C300/3h-R200/6h	713	100	57	-	-	36	7
Pt-Sn/SiO_2	C500/3h-R150/6h	382	100	66	-	-	33	1
Pt-Sn/SiO_2	C500/3h-R200/6h	293	100	79	-	-	21	-
Pt-Sn/SiO_2	C500/3h-R200/3h	235	100	69	-	-	31	-
Pt-Sn/SiO_2	C500/3h-R300/6h	727	100	65	-	-	35	-

S= drying; C= calcination; R= reduction; h= hours; *r_P reaction velocity for initial time of reaction; X_A= Citral conversion; G+N= Geraniol and Nerol; CAL=Citronelal; 3,7OL=3,7 Dimetil octanol; COL= Citronelol.

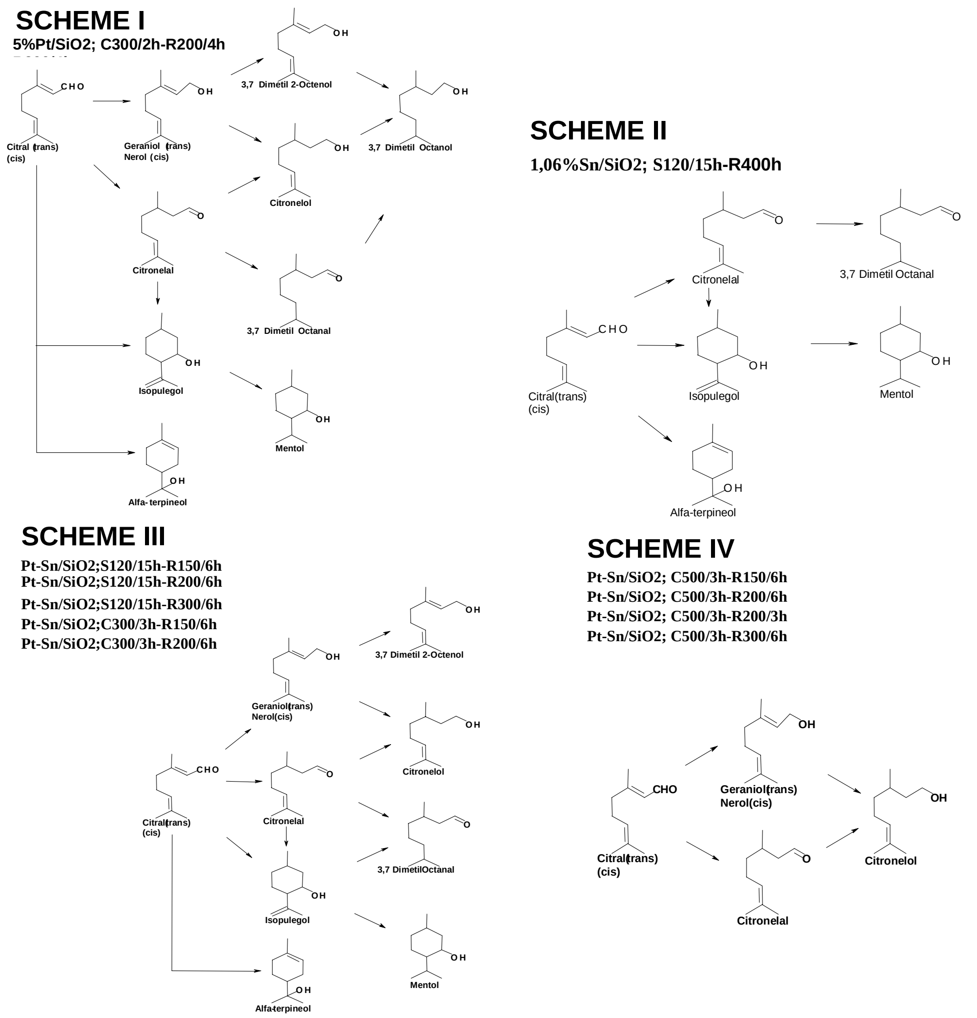


Figure 4 Scheme of reaction of the selective hydrogenation of the citral for 2 hours of reaction: monometallic catalysts Pt/SiO_2 and Sn/SiO_2 and bimetallic catalysts Pt-Sn/SiO_2.

3.3 Effect of promoter Sn

The real content of platinum in catalysts Pt-Sn/SiO_2 was of 4% p/p; it was characterized by Adsorption Atomic. The presence of tin and the metallic particle size between 100-4000 Å were determined by Scanning Electronic Microscopy (SEM). Also with SEM was observed the superficial segregation when the calcination temperature was increased. The diminution of Pt and augment of Sn was observed in the micrographies, which suggested the superficial segregation. Before results shown that the selectivity and activity were improved and increased with the presence of tin as shown in Table 1 and the variation of the composition (%) versus reaction time (h) as shown in Figures 3 (c)-(k). The high conversion obtained with the presence of tin can be associated to a synergetic effect among active agent-promoter-support. The reached maximum conversion was kept constant for calcination and reduction temperature effect in the bimetallic catalysts Pt-Sn/SiO_2 as shown in Table 1.

The schemes III and IV as shown in Figure 4 are resulted of the selective hydrogenation of the citral as shown in Figures (c)-(k), it were resulted mainly by effect of promoter tin and other interaction effects, e.g. Sn-Pt-support-citral-solvent. The reduction temperature of 120°C for the active agent Pt and 530°C for the promoter Sn were found after drying with the Temperature of Programmed Reduction (TPR), after calcination the reduction picks shown a diminution, and after reaction the reduction picks exhibited a change and small size. According to the literature the picks reduction behavior exposed the presence of metals in form metallic, oxides, complexes or interactions weak or strong between metal-support, metal-metal or metal-metal-support. Also the presence of Pt and Sn after preparation, calcination and reduction for catalysts Pt-Sn/SiO_2 suggest the presence of league, difficulty reducible oxides, agglomerates, sinterization, exposed face change and segregation. The scheme IV as shown in Figure 4 is simple and common to the others; it can be used for possible kinetic study of the performance of the selective hydrogenation of the citral.

3.4 Effect of the calcination temperature

As consequence of thermal treatment the catalytic tests shown that citronelal is an intermediary product in the catalysts Pt-Sn/SiO_2 as shown in Figures 3 (c)-(k) principaly. By means of analysis of the Figures 3 (c)-(k) were plotted the results of the Figure 5, it shows the reaction rate (r_P), the conversion (%) and selectivity (%) versus variation of calcination temperature (°C). The high catalytic activity, selectivity and conversion of 100% were obtained by the thermal treatment that were applied to the catalysts Pt-Sn/SiO_2, the conversion was kept constant and the selectivity increased with the calcination and reduction temperature effect as shown in Figure 5. The selectivity and activity results can be studied by different techniques of characterization. In the micrographics of Scanning Electronic Microscopy (SEM) were observed sintering that can be caused by high calcination temperatures. It can be probably according to the literature by the league formation (Coloma et al., 1997), the agglomeration of particles or bulk (Haller and Resasco, 1987), the solution of tin in platinum or platinum in tin (Cimino and Stone, 1975; Lobão et al., 1998), the clusters metal-metal (Haller and Resasco, 1987), the encapsulation of metals in support (Stakheev et al., 1999), the collapse of metal-metal, metal-support or metal-metal-support (Stakheev et al., 1999), the anchoring of metals on the support (Stakheev et al., 1999) or the formation of facets or faceting (Delbeq and Sautet, 1995; Rodriguez, 1996).

The particles size Pt (111) (index Miller) of the catalysts Pt-Sn/SiO_2 as consequence of the thermal treatment effect were found between 79-230 Å by Diffraction of Ray-X (XRD). The silica support exposes a system of tetragonal crystallization where the referential parameter of crystal net is $a_o=b_o=4.971$ Å and $c_o=6.918$ Å, and the experimental parameters were found like a=b=4.496 Å and c=7.319 Å (Mendoza Marin, 2000), these results exhibit the experimental validity of the gel silica. Furthermore the particle sizes for the catalysts Pt-Sn/SiO2 were found between 45-303 Å by Chemisorption (CHE). After preparation the catalysts exhibited the formation of different phases which were found by Diffraction of Ray-X by means of high picks or by significant order like Pt°, $PtSn_4$, $Pt2Sn_3$, PtO_2, etc. These phases changed due to the calcination and reduction temperature effect. Particularly the pick of Pt^o can be found like segregated, isolated or league form with tin. Also the picks Pt (111) were found that the crystal size of platinum were augmenting due to temperature effect, e.g. calcination temperature.

In the isotherms of hydrogen adsorption were found that the connection force between hydrogen and metal particles of platinum decreased when temperature of oxidation increased, also the chemical adsorption were acquiring the performance of physical adsorption with weak league force or probably molecules of hydrogen without dissociation. Before results were found by Chemisorption (CHE). Furthermore the dispersion of the metal Pt, volume of adsorbed hydrogen and specific metallic superficial area were found that diminished when the calcination temperature increase from 120°C/15h to 300°C/3h and 500°C/3h, but the particles size of Pt increased in the same condition. These last results are according with the characterizations of XRD, CHE and literature. From 50 to 900°C were found that the lost mass in the catalysts Pt-Sn/SiO_2 were inversely proportional to the augment of the thermal treatment, these results were found by Termogravimetric analysis (TGA) (Mendoza Marín, 2000).

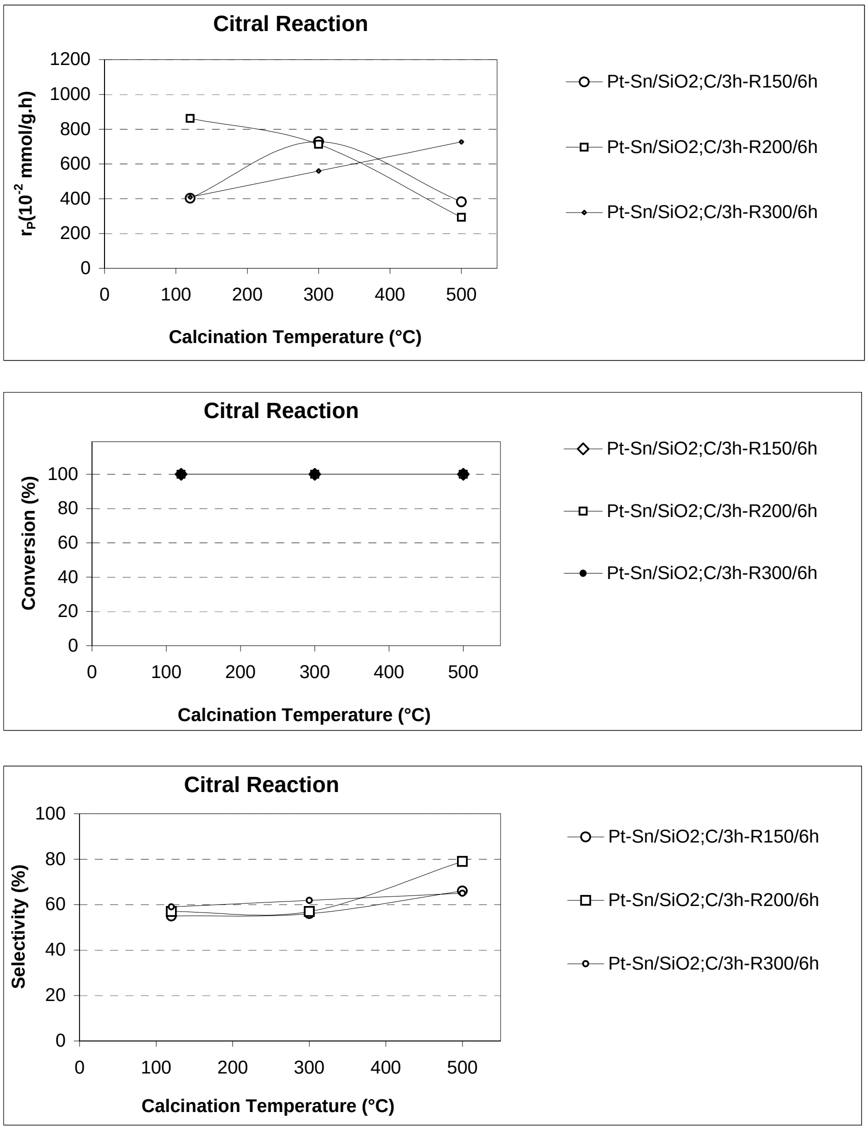


Figure 5 Effect of the calcination temperature for bimetallic catalysts Pt-Sn/SiO_2 in the selective hydrogenation of the citral.

3.5 Effect of the reduction time

The reaction speed (r_P), conversion (%) and selectivity (%) versus time of reduction (h) for catalysts Pt-Sn/SiO_2 are shown in the Figure 6, it is obtained from the slective hydrogenation of the citral as shown in Figures 3 (i) and (j). The catalytic activity increases, the maximum conversion is constant, and the selectivity increases proportionally to the reduction time effect as shown in Figure 6. In this case the absence of reduction picks for catalysts Pt-Sn/SiO_2 were found by the Temperature Programmed Reduction (TPR). It can be attributed according to the literature to the catalyst preparation, the re-oxidation after of the drying, the sintering problems (Wanke et al., 1975), to the phase change, to the superficial segregation (Coq et al., 1991) or superficial oxides. Before results could be responsible by different superficial phenomena like chemical compound of difficulty reduction, the league formation (Coloma et al., 1997), the metallic cluster (Haller and Resasco, 1987), the metallic aggregation (Haller and Resasco, 1987), the solid solution (Cimino and Stone, 1975; Coloma et al., 1997), the sub-oxides species or the coalescence of oxide species (Haller and Resasco, 1987). Then the analyzed results can have effect on the performance of platinum, tin and support, also the metals can be present like metal, oxides, complex or with weak or strong interaction between metal-support, metal-metal or metal-metal-support.

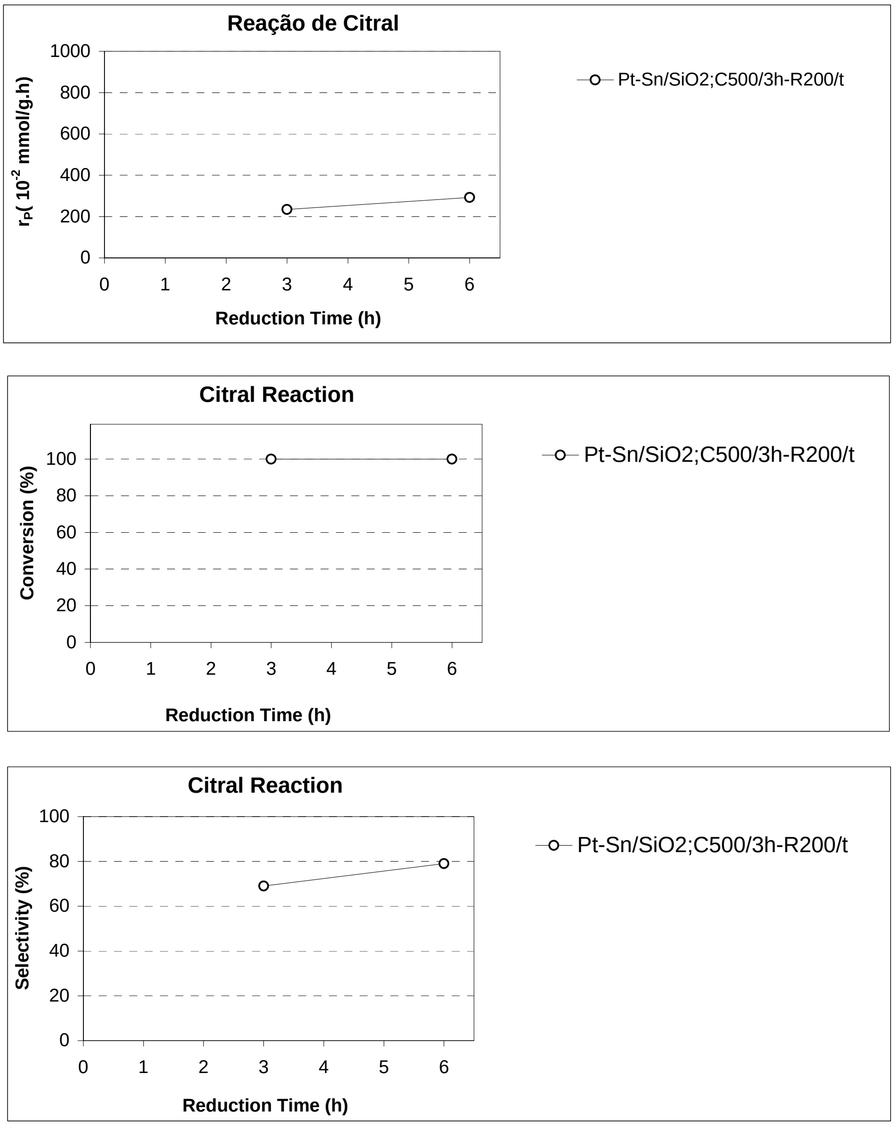


Figure 6 Effect of reduction time for bimetallic catalysts Pt-Sn/SiO_2 in the selective hydrogenation of the citral.

4. Conclusions

The obtained results were associated to the catalyst performance, which can be influenced by the crystal size of Pt (111), it was affected by different thermal treatment, and it were determined between 79-230 Å by Diffraction of Ray-X (XRD), between 45-303 Å by Chemisorption (CHE) and in general the size of metallic phase were found between 100-4000 Å by Scanning Electronic Microscopy (SEM). The reactivity of link C=O may be caused by superficial segregation according to the calcination temperature, by steric phenomenon, by the presence of substitute groups of electrofilic and nucleofilic centers.

The activity and selectivity are influenced by degenerated electronic states that are affected in general by thermal treatment and specifically by calcination temperature. The link σ, the presence of Bronsted and Lewis place, synergetic interaction between active agent-promoter-support-solvent, the superficial segregation of tin and platinum, the presence of phases of Pt^o, $PtSn_4$, Pt_2Sn_3, PtO_2, etc., the presence of phenomenon of particle agglomerations, the solution of tin in platinum or platinum in tin, the presence of metallic clusters, the metal encapsulation in support, the presence of collapse, the presence of metal anchoring on support or facet formation were associated to the variation of the thermal treatment.

The adsorption with reactant dissociation and the formation of intermediate compounds were found in the catalysts Pt-Sn/SiO_2 that lost mass changed inversely to the thermal treatment, it was determined by Thermogravitry Analysis (TGA). Also the league rearrangement or phases , the presence of difficulty reduced chemical compound, the presence of sub-oxide species or coalescence of oxide species could affect the performance of platinum, tin and support by means of the formation and break of league and the product desorption. That were determined by Temperature Programmed Reduction (TPR).

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