Synthesis and properties of PdSn/Al$_2$O$_3$ and PdSn/SiO$_2$ prepared by solvated metal atom dispersed method

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Abstract

A series of solvated metal atom dispersion (SMAD) catalysts: Pd/SiO$_2$, Pd/Al$_2$O$_3$, Sn/SiO$_2$, Sn/Al$_2$O$_3$, Pd$_x$Sn$_y$/SiO$_2$ and Pd$_x$Sn$_y$/Al$_2$O$_3$. It was prepared by simultaneous evaporation of Pd and Sn. The metals were co-deposited at 77 K using acetone, 2-propanol and THF to produce colloids "in situ" all the supported catalyst were characterized by chemisorption, transmission electron microscopy (TEM), thermogravimetric analysis (TGA) and TPR. This series of catalyst were tested for crotonaldehyde hydrogenation in gas phase to obtain crotyl alcohol.
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Keywords: Solvated metal atom dispersion; Catalysis; PdSn/Al$_2$O$_3$; PdSn/SiO$_2$

1. Introduction

The metal catalysts used in the selective hydrogenation of α,β-unsaturated aldehydes are based on Pt, Rh, Ru, Os, Ir, Ni, Co and Pd. From all these metals, the latter is not a good catalyst for selective reduction of the conjugated carbonyl group [1]. In fact, the literature indicates that none of the metals mentioned above exhibit a good selectivity towards the production of the unsaturated alcohol. The selectivity can be improved with the addition of promotors like Sn [2–4] and Ge [5], which can increase dramatically the formation of the unsaturated alcohol. The results shown in the literature reveal that the active species of tin is ionic, in other words, the active form of tin is in the cationic state (Sn^{n+}).

The formation of an alloy with Sn might also help toward selectivity but there is no available literature at this point. Therefore, we considered of interest to prepare a series of PdSn alloy catalysts to determine if they would cause selectivity change.

In this paper, we are discussing catalyst characterization and the results obtained in the crotonaldehyde hydrogenation in the presence of Pd/SiO$_2$, Pd/Al$_2$O$_3$, PdSn/SiO$_2$ and PdSn/Al$_2$O$_3$ prepared by the technique "solvated metal atom dispersion" (SMAD) [6,7]. This method allows the production of very small, zero-valent bimetallic particles. It involves the simultaneous evaporation of the method and their co-condensation with the vapor of a chosen solvent at 77 K.

The technique allows to evaporate simultaneously Pd and solvents (ketones, alcohols or ethers) at 77 K. The colloids are produced "in situ" and reacted with activated SiO$_2$ or Al$_2$O$_3$ previously introduced in the reactor bottom.

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The competence between the solvatation and the clusterization of metal–metal carried out to form a small amorphous particle [8] and to incorporate fragments and/or solvent molecules on the particle surface. These fragments modify dramatically the properties of metallic particles [9,10], but can be removed by heating the solids over 100 °C. The amount of solvent incorporated depends on the metal and solvent [11,12]. In these catalysts, for example, the weight loss is only around 3%, in the bimetal supported either SiO_2 or Al_2O_3. Li and Klabunde [6] have prepared the system Pt–Sn prepared in SiO_2 and Al_2O_3 by SMAD method and they also found that most of the Sn (84%) was Sn^0, but Sn^{2+} and Sn^{4+} were also present. After an extremely oxidation treatment some Sn^0 still remained, showing that it was deeply alloyed with the Pt. This is different from conventional catalyst, where if any Sn^0 is present, it is on the system and is easily oxidized [7,13].

In this work, we study the influence of Sn^0 and the possible influence of the organic fragment incorporated on the surface of the particles, in the systems Pd/SiO_2, Pd/Al_2O_3, $PdSn/SiO_2$ and $PdSn/Al_2O_3$ obtained from acetone, 2-propanol and THF. Also, we report the full characterization of the dispersed particles by transmission electron microscopy (TEM), electron diffraction, metallic area, thermogravimetric analysis (TGA) and TPR and finally, the catalysts were tested in the crotonaldehyde hydrogenation to obtain crotyl alcohol.

2. Experimental

The catalyst formation was carried out in a bimetal reactor atom [14]. Two tungsten crucibles (W–Al_2O_3 from Sylvania Emissive) were charged with around 0.0872 g of Pd and 0.0137 g Sn metal in lumps. Distilled and dried solvents (e.g. 100 ml 2-propanol) were in a ligand inlet tube and freeze–pump–thaw degassed for five cycles. The reactor is kept under vacuum until reaching 5–10 μm of Hg, previously the active Al_2O_3 (4.9987 g) has been introduced with a magnetic stir bar.

A liquid nitrogen filled dewar was placed around the vessel and Pd, Sn and 100 ml 2-propanol (acetone or THF) were co-deposited over a 1.5 h period. The matrix was of a black color at the end of the co-deposition.

The matrix formed was allowed to warm slowly for 1.0 h at room temperature under vacuum by removal of the liquid nitrogen dewar. Upon meltdown, the black dispersion was allowed to warm for another 0.5 h at room temperature under $N_2(g)$ flow. Finally, the metal dispersed in solvent is stirred with Al_2O_3 for 24 h in the reactor at room temperature under $N_2(g)$.

For acetone and 2-propanol as solvents, highly stable colloids with a narrow particle size distribution were obtained. On the contrary, THF formed unstable colloids of broader size distribution. these solvents were compared to determine if there was any influence of the colloids properties on the catalytic behavior during the hydrogenation of crotonaldehyde.

2.1. Transmission electron microscopy

Electron micrographs were obtained on a JEOL JEM 1200 EXII. The supported catalyst is grounded in an agate mortar and dispersed in 2-propanol or acetone. A drop of each dispersion was placed on a 150 mesh copper grid coated with carbon. Several magnifications were used. Four to five electron micrographies in different places of the copper grid were taken. Then 80–100 particles in each micrography were measured. Finally, the 6.0 Origin program (Microcal Software Inc.) was used to plot the frequency histogram to determine the mean particle size.

2.2. Selection area electron diffraction (SAD)

The electron diffraction of catalyst was obtained in the JEOL microscope internally calibrated with gold standard (Merck, 99.99% of purity; 120 kV, $K = 3.848$ cm Å). The diffraction patterns were obtained using an aperture of the limitant field of 20 μm. In this way, the diffractions coming from the grid are avoided and the observed area is minimized.

2.3. Thermal studies

The thermogravimetric studies on the catalyst were carried out using a Perkin-Elmer TGA-7. The weights of the samples were in the range of 5–10 mg. The sample pan was placed in the balance system and the temperature was increased from 25 to 550 °C at a heating

rate of 10 °C/min. The weight of the sample pan was continuously recorded.

2.4. Chemisorption

Hydrogen chemisorption at 343 K was carried by a pulse method in a TPD/TPR 2900 Micromeritics system provided with a thermal conductivity detector. Before the experiments the samples were reduced in situ under hydrogen flow (50 cm^3/min) at 673 K for 1 h. Then the gas was shifted to Ar and kept at this temperature for 2 h and cooled down to 343 K. Once the baseline was restored, different pulses of H$_2$ were sent to the sample holder, up to complete saturation of the metallic surface. By evaluating the amount of H$_2$ uptake at 343 K, the H/Pd ratio was obtained.

2.5. Hydrogenation of crotonaldehyde

The crotonaldehyde hydrogenation was carried out in a glass flow reactor, where 10 mg of catalyst ground in a mortar to produce powder were placed over a glass frit. Previous to the evacuation the samples were treated in H$_2$ at 373 K for 1 h and then cooled down up to 323 K. Then the reactant mixture

(H$_2$/crotonaldehyde = 26, flow rate = 100 cm^3/min) was fed into the reactor. The analysis of the reactants and products were carried out by on line mass spectrometer HIDEN HAL 200.

The reactor was kept in a furnace stabilized at 50 °C, a mixture of hydrogen and crotonaldehyde was maintained using a flow rate of 100 cm^3/min, the pressure p^0 of crotonaldehyde was 11.3 mm of Hg and the total pressure was 1 atm. The gases were collected and analyzed in a HNU 321 gas chromatograph provided with a Spectra Physics model SP4270/4290 integrator.

3. Results

Scheme 1 summarizes the process in the SMAD reactor, for catalyst preparation.

3.1. Electron microscopy and electron diffraction

In Table 1, the sizes obtained from the TEM are summarized (Figs. 1 and 2). In general, the size of the dispersed particles on Al$_2$O$_3$ are bigger than those supported over SiO$_2$. These sizes are comparable to the monometallic and bimetallic unsupported colloids
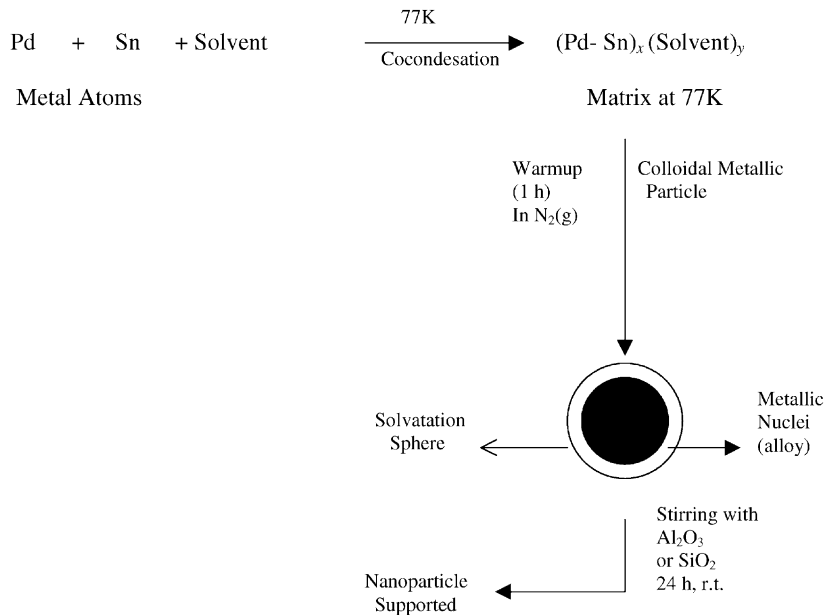
Scheme 1.

Table 1
Particle size of PdSn supported over SiO_2 and Al_2O_3

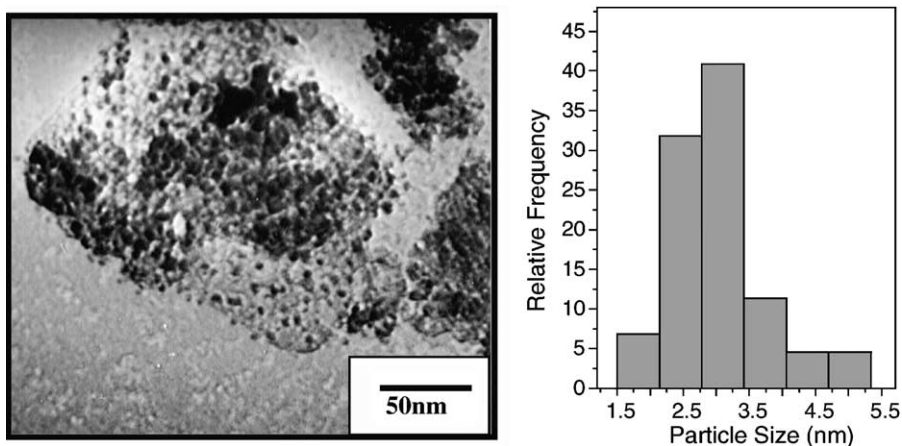| PdSn/Al_2O_3			PdSn/SiO_2			Solvent
Sn/(Pd + Sn)	Average particle size (nm)	S.D. (nm)	Sn/(Pd + Sn)	Average particle size (nm)	S.D. (nm)	
0.5	16	6.0	0.5	2.0	0.7	Acetone
0.1	4.0	0.6				
1.0	5.0	1.0	1.0	4.0	1.0	2-Propanol
0.7	3.0	0.7	0.7	8.0	4.0	
0.3	8.0	2.0	0.3	3.0	0.4	
0.0	5.0	2.0	0.0	5.0	1.0	
0.2	14	6.0	0.2	9.0	4.0	THF
	41	12				

Fig. 1. Topographic image: catalyst, (PdSn/Al_2O_3)–2-propanol; Sn/(Pd + Sn), 0.7.
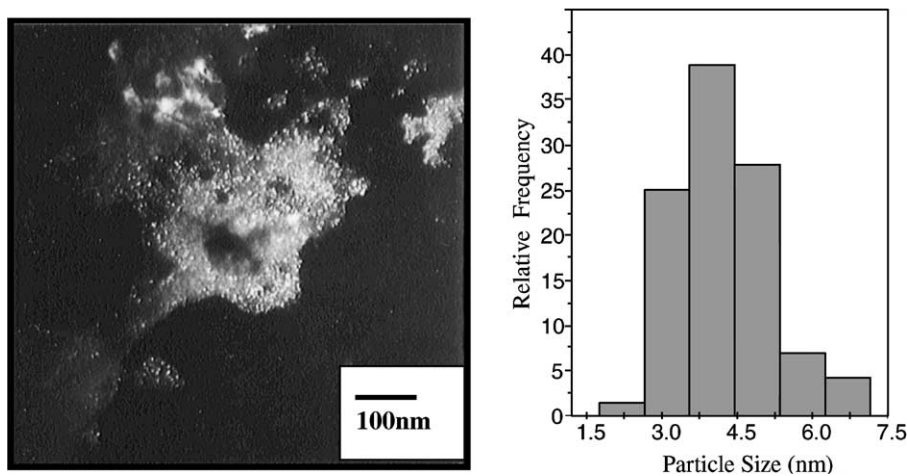

Fig. 2. Dark field micrograph: catalyst, (PdSn/Al_2O_3)–acetonaldehyst; Sn/(Pd + Sn), 0.1.

obtained by this method in different organic solvents [15–17]. It is evident that particles grow mainly during the warming process.

It is well known that Al_2O_3 is a support characterized by the strong metal–support interaction modifying the electronic properties of metallic particles [18,19] while SiO_2 is a more inert support [20]. The difference in size between both the supports is attributed to the different interactions between the support and the particles.

The bimetallic particles of PdSn dispersed from acetone in SiO_2 and Al_2O_3 showed similar sizes. On the contrary, the dispersed particles on the supports from the THF dispersions present a wider size distribution and the particles are bigger than 8 nm (Table 1). This result is in agreement with the characteristic of metallic dispersions produced in this solvent. Practically, most of the dispersions are less stable and the sizes obtained are bigger than the most stable systems, disclosing the low solvatation power of the solvent [21].

It is known that the addition of an inert second metal can change the chemical/catalytic properties of metal supported Pt group [22]. To determine if high temperature would affect these catalysts, two samples of $PdSn/Al_2O_3$ prepared from 2-propanol with Sn atomic fractions 0.2 and 0.7 were kept at $400\,^\circ C$ under vacuum for 1 h (10 μm of Hg). The results demonstrated that particles with a higher content of Sn tended to grow to a greater extent than the particles with less content of Sn. In Fig. 3a and b, the micrographs of

the catalyst with a fraction of 0.7 are shown. Initially, the size is 3 nm and after the thermal treatment we observed particles of 50 and 6 nm (Fig. 3b). On the contrary, in the system with the fraction 0.2, the histogram reveals the presence of two particle sizes with an average of 4 and 9 nm (the initial size was 4 nm). Even then we could not get the particle composition in full extent and it is evident that the presence of a greater amount of Sn induced bigger particle formation.

3.2. Electron diffraction

Most of the colloidal particles obtained by the SMAD method show low crystallinity with the exception of silver [23]. On the other hand, the supported bimetallic particles are more crystalline than their non-supported homologs. It is interesting to notice that monometallic particles of Pd and Sn supported are less crystalline than their bimetallic homologs. Due to the presence of several phases and the presence of the support, it is difficult to be sure, with a simple diffraction in a CTEM, the exact nature of the particles, however, it is possible to detect Pd–Sn, hexagonal and orthorhombic, respectively, Pd^0, Sn^0 and some tin oxides (Table 2). The combination between the electron diffraction and dark field images helps to determine qualitatively the amount of some phases, Fig. 4a and b are images of dark field carried out in the reflection $\{1\,0\,1\,2\}$ of PdSn hexagonal ($d_{hkl} = 3.21\,Å$) and $\{2\,0\,0\}$ of de-Pd ($d_{hkl} = 1.95\,Å$)

(a)   (b)
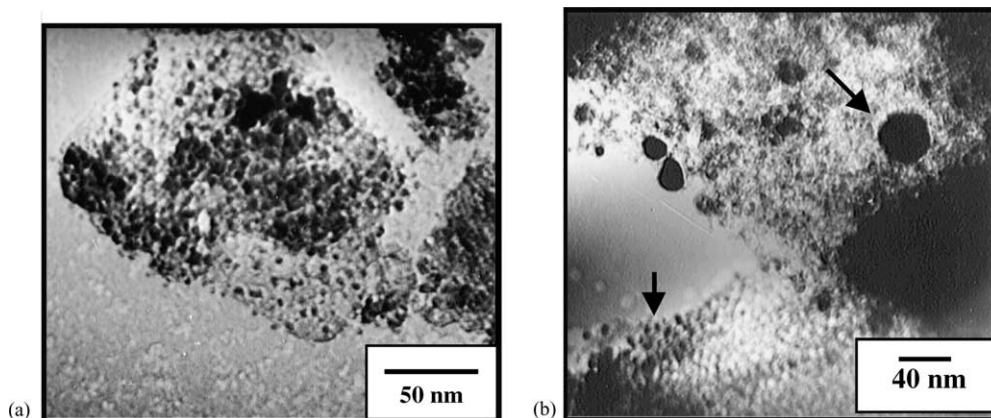
Fig. 3. (a) Topographic image: Sn/(Pd + Sn), 0.7; (PdSn–2-propanol)/Al_2O_3; (b) bright field micrograph of Sn/(Pd + Sn), 0.7; heated at $400\,^\circ C$ under vacuum.

Table 2
Electron diffraction pattern of the (PdSn–2-propanol/Al$_2$O$_3$) catalyst

Ring	Ring diameter	d_{hkl} (Å)	$h k l$	Phase	Table date (Å)
1	1.20	3.21	{1 0 1 2}	PdSn hexagonal	3.16
2	1.96	1.95	{2 0 0}	Pd^0	1.94
3	2.40	1.60	{2 1 1}	SnO Th.	1.60
4	3.34	1.15	{1 0 4}	SnO T.	1.15

Sn/(Pd + Sn): 0.7.

(Table 2). In Fig. 4a, it can be observed that particles of PdSn are hexagonal and particles are rich in Pd^0. Moreover, of this phases, the pattern of diffraction reveal the presence of SnO (d_{hkl} = 1.60 and 1.15 Å, Table 2). It is important to mention that oxide formation is very low in these systems and they are very stable to oxidation (TPR analysis).

3.3. Thermal analysis

The solids obtained by the evaporation of the solvent present a different amount of solvents incorporated, which can be eliminated by heating under vacuum. The amounts of solvent depend on the metal and the solvent used in the reaction [12]. Table 3 presents the decomposition temperature of the catalyst PdSn/Al$_2$O$_3$ and PdSn/SiO$_2$ prepared from the dispersions in acetone, 2-propanol and THF (e.g. Fig. 5).

If we compare the thermal decomposition (T_D) for the same solvent and the composition in both supports (Table 3), the decomposition temperature is higher in alumina than in silica, which reveals that the interaction between the supports and the dispersed particles is different in both the supports. The interaction between the metallic particle and the support changes the morphology and electronic properties of the particles. The property of the latter can induce the formation of particles with excess or with electron deficiency [10]. The formation of metallic particle electron deficient on Al$_2$O$_3$ has been reported for Pd [18] and Pt [19]. This could be demonstrated as the difference in the T_D between both catalyst is produced by the difference in the properties of the supported particles in each support.

The T_D for Pd–Sn catalyst supported on Al$_2$O$_3$, prepared in 2-propanol tends to increase with the increase of Pd content (Table 3). However, SiO$_2$ decreases as
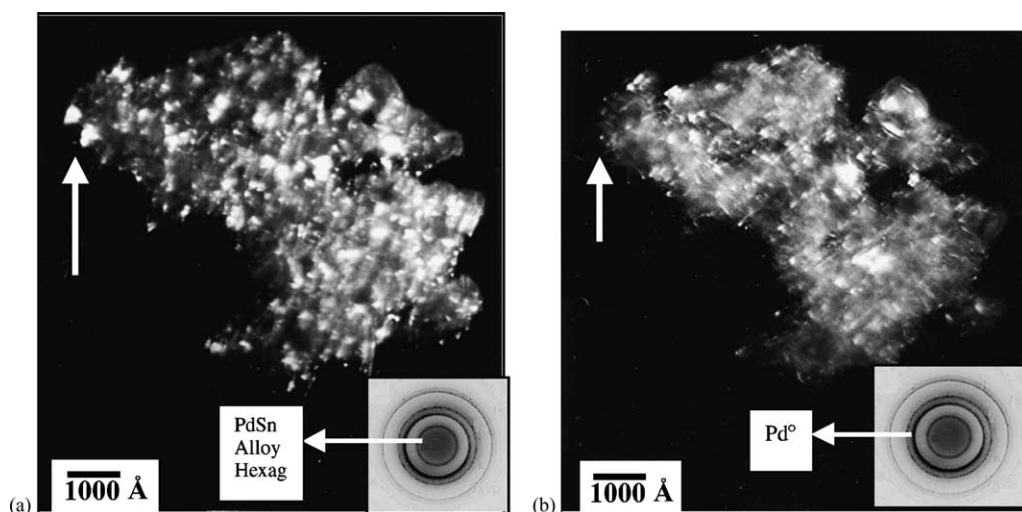

Fig. 4. Dark field: (a) reflection {1 0 1 2}, PdSn, hexagonal; (b) reflection {2 0 0}, Pd^0.

Table 3
Thermal analysis of bimetal catalyst supported in Al_2O_3 and SiO_2

PdSn/Al_2O_3			PdSn/SiO_2			Solvent
Sn/(Pd + Sn)	T_D (°C)[a]	Weight loss (%)	Sn/(Pd + Sn)	T_D (°C)[a]	Weight loss (%)	
1.0	53.8	2.5				Acetone
0.5	61.0	3.2	0.5	59.9	2.5	
0.1	107	2.7				
0.0	68.1	1.2				
1.0	63.9	1.3	1.0	72.0	1.9	2-Propanol
0.7	71.1	2.1	0.7	57.6	3.9	
0.2	69.2	2.9	0.3	66.0	2.7	
0.0	72.9	1.3	0.0	62.5	2.4	
0.2	108.4	3.2	0.2	82.7	8.4	THF

[a] Main decomposition temperature.

Pd content increases (e.g. 2-propanol) demonstrating that the behavior of the PdSn particles present in the catalyst behave differently both in Al_2O_3 and SiO_2. The behavior of PdSn/Al_2O_3 catalyst prepared from acetone showed a less predictable behavior. This is mainly due to the condensation of acetone over metals like Au and Pd producing some dehydrogenation, dehydration and/or CO less, which has been reported by Cárdenas and Klabunde [24,25]. The catalyst formed in 2-propanol exhibit a point that does not follow the linear tendency of an increase of T_D with the increase of Pd content, but it is clear that there is an increase in the decomposition temperature, T_D, with respect to the Sn/Al_2O_3 catalyst.
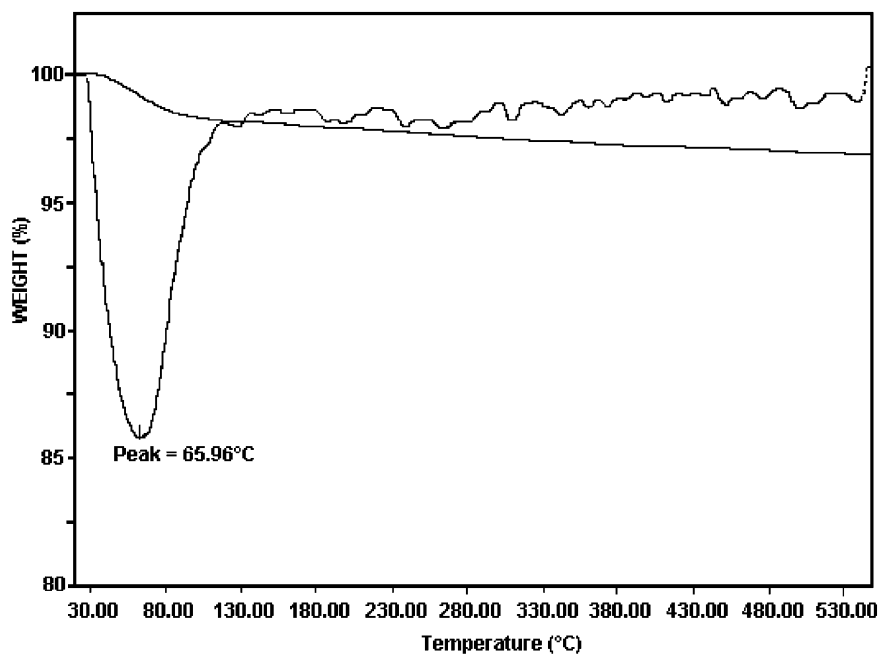

Fig. 5. TGA of (PdSn–2-propanol)/SiO_2; Sn/(Pd + Sn), 0.3.

Table 4
Metallic area, H/Pd of bimetallic catalyst supported in SiO_2 and Al_2O_3

PdSn/Al_2O_3				PdSn/SiO_2			
Sn/(Pd + Sn)	Area (m^2/g of Pd)	H/Pd	Solvent	Sn/(Pd + Sn)	Area (m^2/g of Pd)	H/Pd	Solvent
0.0	11	2	2-Propanol	0.0	10	2	2-Propanol
0.1	11	3	Acetone	0.2	15	3	THF
0.2	3	1	THF	0.3	14	3	2-Propanol
0.3	7	2	2-Propanol	0.5	1	0.2	Acetone
0.5	13	3	Acetone	0.7	2	0.5	2-Propanol
0.7	18	4	2-Propanol	1.0	–	–	2-Propanol
1.0	–	–	2-Propanol				

3.4. Chemisorption

Metal dispersion and particle size for some mono-metallic and bimetallic catalysts from H_2 chemisorption data were evaluated. Metal particle size was estimated from the equation $d = 5/S\rho$, where S is the metallic surface and ρ the specific gravity. It was assumed that the crystal possesses cubic shapes with five faces exposed to hydrogen and the other one to the support. Previous experiments have shown that H_2 is not absorbed on Sn, therefore, the H_2 uptake occurs only on Pd surface.

In Table 4, the metallic area, the dispersion (H/Pd ratio) and the sizes obtained by chemisorption of H_2 and by TEM are shown. The dispersion (H/Pd ratio) of particles with both supports is not bigger than 3 on average. It can be observed that H/Pd chemisorption rather of the Pd particles is lightly lower than the bimetallic of PdSn particle for both the supports, which is opposite to that observed in the catalyst prepared by traditional impregnation methods, where the Sn covers the Pd and the surface area decreases (also H/Pd ratio).

This behavior can be attributed to metal atom nucleation effects that occur during the reaction. As a consequence, independent particles richer in Pd or Sn are produced and a few bimetallic particles of Pd_nSn_m alloys are produced. In summary, when Al_2O_3 is the support, it is probable that at a relatively low Sn amount the alloy with Pd is forming, an independent particle, but does not form core/shell particles, where Sn is the shell. However, when SiO_2 is the support, Sn apparently tends to cover the Pd particles.

The low dispersion may be attributed to a partial coverage of Pd particles by SnO_x species. Similar behavior has been reported by Völter et al. [26] and Palazov et al. [27] for alumina supported Pt–Sn catalyst, by Coloma et al. for Pt–Sn/C catalyst [28] and by Reyes and co-workers for Rh–Sn catalysts [29] and due to the presence of organic materials, the particles behaves as pseudo-organometallic. The presence of organic fragment and/or carbon could avoid the chemisorption of hydrogen [30]. This could explain the difference between the size obtained by TEM and the chemisorption of H_2 (Table 5).

3.5. Hydrogenation of crotonaldehyde

Tables 6 and 7 reveal that the main products of crotonaldehyde hydrogenation over Pd/SiO_2, Pd/Al_2O_3 and the bimetallic systems of PdSn are butyraldehyde (main product, 73–89%), crotyl alcohol (12–23%) and a lower percentage of butanol. For higher percentage of Sn, it can be observed the hemiacetal formation (4-butoxy-4-etoxy-2-butyne, $M_w = 144$ g/mol).

After 2 h, a small degradation of the catalysts was observed. This deactivation is probably due to the poisoning of the active sites by crotonaldehyde decarbonylation. However, in general the catalysts show a high level of conversion.

There are three important facts to be considered:

(i) The SMAD Pd catalysts show a relatively high selectivity to crotyl alcohol compared with conventional catalysts [31].
(ii) The addition of Sn^0 to the SMAD catalyst gave only a slight increase in their selectivity (Tables 6 and 7).

Table 5
Chemisorption size and TEM

PdSn/Al$_2$O$_3$			PdSn/SiO$_2$			Solvent
Sn/(Pd + Sn)	Chemisorption (nm)	TEM (nm)	Sn/(Pd + Sn)	Chemisorption (nm)	TEM (nm)	
0.5	34	16	0.5	399	2.0	Acetone
0.1	39	4.0				
1.0	–	5.0	1.0	–	4.0	2-Propanol
0.7	24	3.0	0.7	305	8.0	
0.3	63	8.0	0.3	209	3.0	
0.0	41	5.0	0.0	44	5.0	
0.2	137	14	0.2	31	9.0	THF
		41				

Table 6
Crotonaldehyde hydrogenation catalyst Pd–Sn/Al$_2$O$_3$

Sn/(Pd + Sn)	Conversion (%)	Selectivity (%)			Acetaldehyde (%)	Solvent
		Bu-H	Bu-OH	Crot. Al.		
0.0	100	79	5	16	0	2-Propanol
0.1	78	85	0	15	0	Acetone
0.2	39	80	0	20	0	THF
0.3	100	79	3	18	0	2-Propanol
0.5	75	77	0	23	0	Acetone
0.7	18	89	6	0	5	2-Propanol
1.0	6	50	40	0	10	2-Propanol

Bu-H, butyraldehyde; Bu-OH, n-butanol; Crot. Al., crotyl alcohol.

(iii) The SMAD catalysts give less saturated alcohol compared to the conventional catalysts.

Ponec [1] has reported that Pt supported catalyst, which exhibit a low selectivity to crotyl alcohol (near 10%), when is promoted with Sn and increase of about 30% is observed. Reyes and co-workers [29] have studied the hydrogenation of acronaldehyde in liquid phase, they reported that Rh/SiO$_2$ catalyst exhibit a selectivity of 2% over the insaturated alcohol when Sn is added in greater amount than 30% (exactly 37%). On the contrary, the hydrogenation of crotonaldehyde on Pd/C only gives the saturated aldehyde. When FeCl$_2$ was added on Pd/C, this gives 100% saturated

Table 7
Crotonaldehyde hydrogenation catalyst Pd–Sn/SiO$_2$

Sn/(Pd + Sn)	Conversion (%)	Selectivity (%)			Acetaldehyde (%)	Solvent
		Bu-H	Bu-OH	Crot. Al.		
0	62	75	7	18	0	2-Propanol
0.2	46	85	0	15	0	THF
0.3	67	81	6	13	0	2-Proapnol
0.5	7	80	0	0	20	Acetone
0.7	3	80	0	0	20	2-Propanol
1.0	7	82	0	0	18	2-Propanol

Bu-H, butyraldehyde; Bu-OH, n-butanol; Crot. Al., crotyl alcohol.

aldehyde [32]. Pd is know to be a poor catalyst for hydrogenation of the C=O bonds, this is attributed to that the best adsorption form is the η_4 or di-π η_2 [32].

The presence of organic fragments on the Pd particles should modify their electronic and steric properties [8,31]. The higher selectivity observed by the SMAD Pd particles should be attributed to a modification in the way crotonaldehyde is adsorbed, although the details of this effect are unclear.

We have mentioned that the addition of Sn^0 does not increase the selectivity of this catalyst significantly. This can be attributed to the absence of Sn^{n+}, which
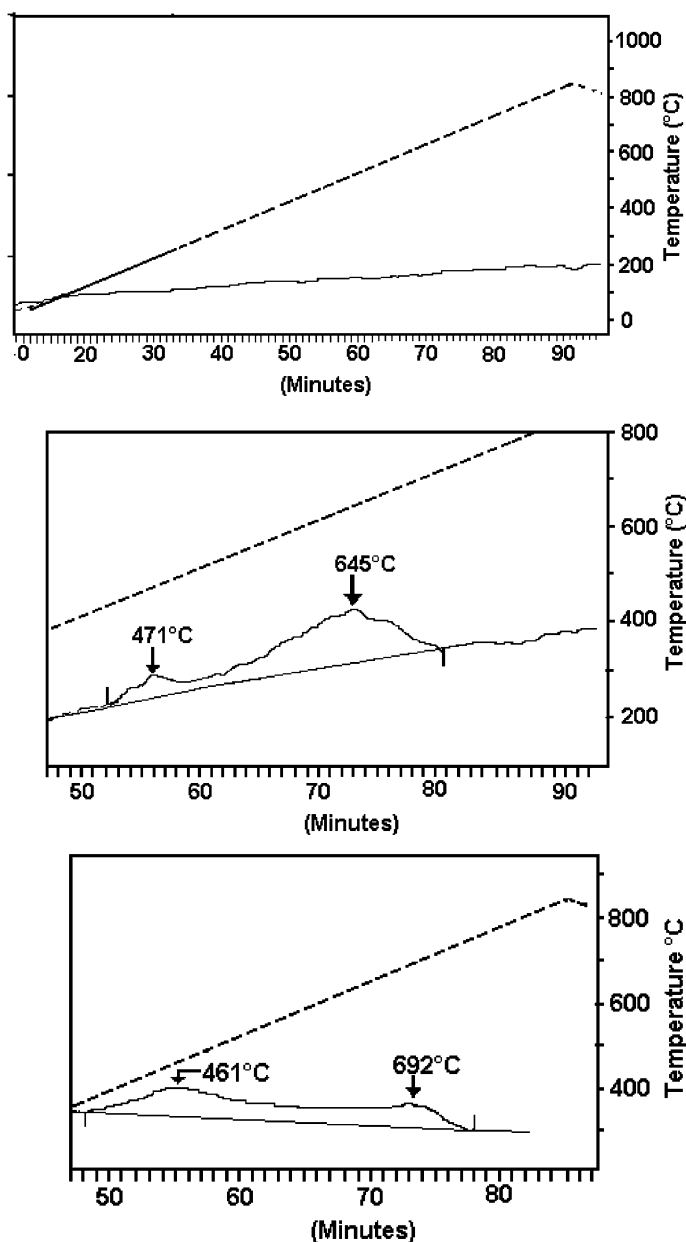

Fig. 6. Sequence of the TPR $\to$ TPO $\to$ TPR Sn/SiO$_2$ catalyst.

is believed to be an active modifier [3–5]. The absence of this modifier in the catalyst can be deduced from the TPR measured in the catalyst of Sn/SiO$_2$, in which no reduction peak was observed (Fig. 6). On the contrary, the TPO shows a main oxidation peak at 645 °C and another at 471 °C. This is evident in the catalysts mentioned previously in which Sn is zero-valent.

4. Conclusions

(1) We have shown that SMAD Pd catalyst exhibits a higher selectivity to carbonyl reduction in crotonaldehyde than to conventional Pd catalysts. Although the reason for this is unclear, probably is related to residual solvent fragment on the Pd surface that affects the adsorption of the aldehyde.
(2) The addition of Sn^0 has a small effect toward increasing this selectivity. However, a general conclusion is that Sn^0 is not a very effective modifier. Thus, the literature interpretation, that Sn^{n+} is the true modifier, is probably correct.
(3) The hydrogen adsorption/Pd dispersion data indicates that the support (Al$_2$O$_3$ or SiO$_2$) has a substantial influence on the structure of the metal particles formed (Pd^0, Sn^0, Pd–Sn^0) by the SMAD Process.

Further work is necessary to clarify this interesting finding.

5. Summary

Pd and Sn atoms were co-condensed separately and also simultaneously using organic solvents (acetone, 2-propanol and THF) at 77 K. Several catalysts of palladium, tin and bimetal Pd/Sn were deposited on silica and alumina by SMAD technique, using several proportions of Pd and Sn.

The metal and bimetal clusters supported in SiO$_2$ or Al$_2$O$_3$ were characterized by TEM, electron diffraction, TGA, surface metallic area. The test for hydrogenation of crotonaldehyde was carried out.

The particles prepared using this method showed a metal particle size between 3 and 8 nm for PdSn/SiO$_2$ and between 3 and 5 nm for PdSn/Al$_2$O$_3$ prepared either from 2-propanol or acetone. The catalyst prepared

from THF yielded a size between 8 and 14 nm. It was found that the Pd/Sn ratio did not affect strongly the particle size, either with Al$_2$O$_3$ or SiO$_2$. The metallic particles detected were the alloy PdSn, Pd^0, Sn^0 and a low amount of tin oxide.

The TGA carried out on these catalysts shows the incorporation of solvent and/or solvent fragments, which decreased in about 3 wt.%. The desorption temperatures are dependent on the Pd/Sn ratio and the support used.

The hydrogenation of crotonaldehyde in gas phase in the presence of PdSn/SiO$_2$ and PdSn/Al$_2$O$_3$ produced mainly butyraldehyde (73–89%), crotyl alcohol (16–23%) and a small amount of n-butanol. The selectivity to the formation of the desired product crotyl alcohol increased slightly with the addition of tin, but catalyst activity went to zero as the tin loading became larger.

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