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Bimetallic PtSn/C catalysts obtained via SOMC/M for glycerol steam reforming



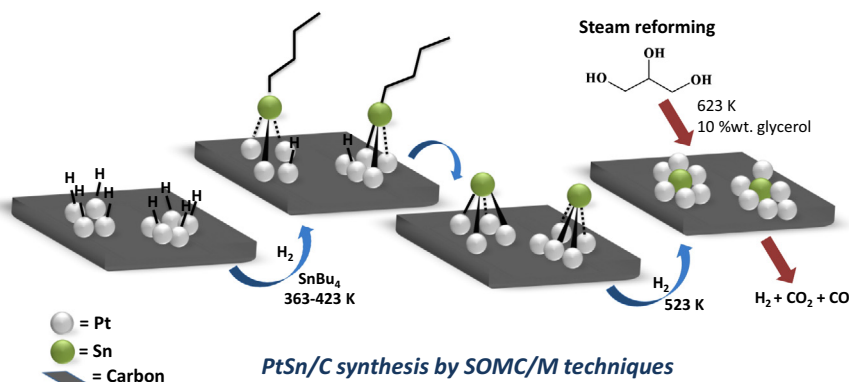
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GRAPHICAL ABSTRACT



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ABSTRACT

A detailed study on the preparation of bimetallic PtSn/C catalysts using surface-controlled synthesis methods, and on their catalytic performance in the glycerol steam reforming reaction has been carried out. In order to obtain these well-defined bimetallic phases, techniques derived from Surface Organometallic Chemistry on Metals (SOMC/M) were used. The preparation process involved the reaction between an organometallic compound ((C₄H₉)₄Sn) and a supported transition metal (Pt) in a H₂ atmosphere. Catalysts with Sn/Pt atomic ratios of 0.2, 0.3, 0.5, and 0.7 were obtained, and characterized using several techniques: ICP, H₂ chemisorption, TEM and XPS. These systems were tested in the glycerol steam reforming varying the reaction conditions (glycerol concentration and reaction temperature). The best performance was observed for the catalysts with the lowest tin contents (PtSn0.2/C and PtSn0.3/C). It was observed that the presence of tin increased the catalysts' stability when working under more severe reaction conditions.

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1. Introduction

During the last decades, the increased energy demand and the need to replace fossil fuels with renewable energy has promoted the production of biodiesel as an alternative fuel with large environmental benefits. Biodiesel is a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats [1–3]. Biodiesel is produced through a base-catalyzed transesterification reaction that leaves behind glycerin as the main by-product.

Despite the large number of current applications of glycerol (cosmetics, pharmacy, food, etc.), the development of biodiesel production has generated a huge increase in glycerol stock since its production is equivalent to ca. 10 wt.% of the total biodiesel produced. For this reason, new uses of this polyol are required in order to enhance the profitability of biodiesel production [4,5].

In the field of heterogeneous catalysis, numerous studies on the rational design of solid catalysts for the selective conversion of glycerol have been developed. However, the high and varied chemical reactivity of this compound often hinders obtaining good selectivity to the desired product (Fig. 1). Additionally, it should be mentioned that the glycerol industrially obtained as a by-product of biodiesel production is actually a mixture of glycerol (80 wt.%), water (15 wt.%) and soap (5 wt.%), and the presence of water in the mixture may damage the catalytic active sites [6]. Therefore, obtaining suitable catalytic systems and determining the optimal reaction conditions are a great challenge.

One of the most interesting routes for the valorization of glycerol is its catalytic reforming. This process allows the transformation of an aqueous glycerol solution into a gaseous stream of CO, CO₂ and H₂ when supported metal catalysts are employed. In the catalytic reforming, the reaction conditions and catalysts can be selected in order to produce syngas for the F-T process or methanol synthesis [7]. Besides, H₂-rich streams can be obtained by coupling the reforming process with the water–gas shift reaction (Fig. 1) [8].

For more than five decades, supported bimetallic catalysts have been widely used in refining, petrochemistry and fine chemistry processes. It is well-known that the second metal may influence the first one through electronic interactions or by modifying the architecture of the active site. Frequently, the interactions between the two metals are complex and unknown, and consequently the preparation procedure influences the nature of the catalytic system obtained [9].

There are different strategies for obtaining bimetallic systems [3]. One of these are the methodologies derived from the Surface Organometallic Chemistry on Metals (SOMC/M) [9]. By applying these techniques it is possible to prepare not only relatively well-defined catalysts that may be alloys of a given composition, but also catalysts in which adatoms of main group elements may be located on the surface of transition metal particles or “organometallic fragments” that are adsorbed on that same surface, thereby improving the activity and/or selectivity of the monometallic catalytic systems.

The addition of tin as promoter has been extensively studied in reactions such as hydrogenations in the field of fine chemistry, alkane dehydrogenation and methane reforming. In all cases it has been observed that the addition of Sn significantly improved the catalytic activity, selectivity and/or stability [10,11]. In this paper we report the systematic study of the effect of tin content on the activity, selectivity and stability of Pt/C catalysts modified with SnBu₄ that have been employed in the glycerol steam reforming reaction. In order to obtain well-defined bimetallic phases, surface-controlled reactions derived from SOMC/M techniques were used in the preparation of the catalysts.

2. Experimental

2.1. Catalyst preparation

A commercial activated carbon (RGC-30), with a high surface area (1598 m² g^{−1}), was used as support. The monometallic Pt/C catalyst was prepared by impregnating the support with an acetone solution (10 mL per gram of support) of H₂PtCl₆·6H₂O (Sigma–Aldrich 99.5%) with the appropriate concentration to obtain a Pt loading of about 5 wt.%. After stirring for 12 h, the excess solvent was slowly evaporated at 313 K under vacuum. Then, the sample was dried at 383 K until complete removal of the solvent, and finally reduced under flowing H₂ at 523 K for 2 h.

Bimetallic PtSn catalysts were prepared by controlled surface reactions, using SOMC/M derived techniques [9]. According to this procedure, the previously reduced monometallic Pt catalyst was reacted with a solution of SnBu₄ (Sigma–Aldrich 93%) in a paraffinic solvent. The reaction was carried out in H₂ flow for 4 h at 363, 393 or 423 K (using *n*-heptane or *n*-decane as solvent) depending on the amount of tin added. After the reaction had finished, the liquid phase was separated and the resulting solid was

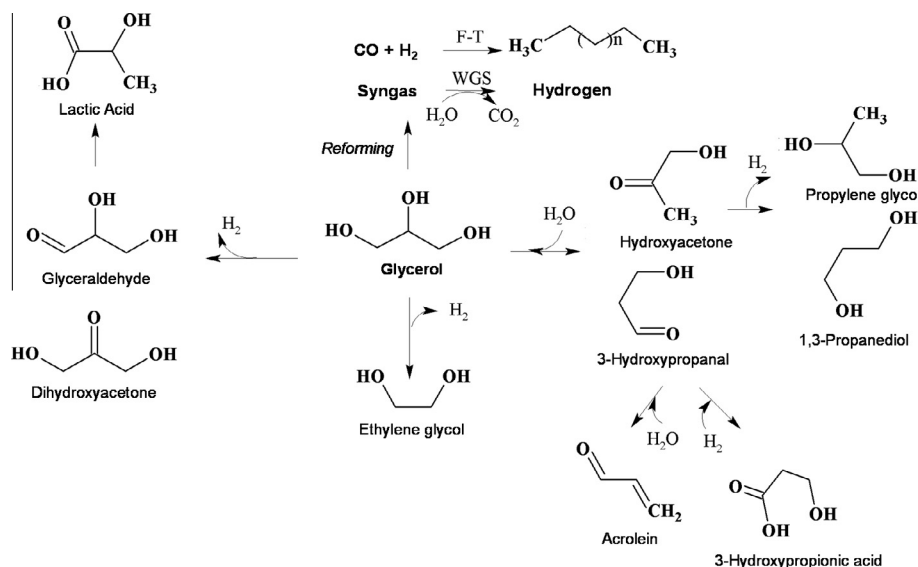


Fig. 1. Different paths for glycerol conversion.

washed repeatedly with *n*-heptane in He flow and subsequently dried in He at 378 K. The solids obtained after this procedure, identified as organobimetallic catalysts (PtSn-OM), still had butyl groups grafted to the surface. The bimetallic phases (PtSn-BM) were obtained by elimination of the organic groups under flowing H₂ at 523 K for 2 h. The bimetallic catalysts obtained are designated PtSn_y/C, where *y* (0.2, 0.3, 0.5, 0.7) represents the Sn/Pt atomic ratio.

2.2. Catalyst characterization

The Pt content of Pt/C and PtSn_y/C catalysts was determined by burning off the catalysts in air at 1073 K and analyzing the residue (dissolved in *aqua regia*) by ICP-OES (Perkin Elmer, Optima 4300 DV). Unfortunately, the analysis method used did not allow for the determination of the tin content due to the volatility of the SnCl₄ formed during the digestion process. Thus, an indirect method was used based on the difference in concentration of the organometallic compound before and after completion of the reaction, determined by chromatographic analysis.

Conventional TEM analysis was carried out with a JEOL JEM-210 model electron microscope working at 200 kV and equipped with an INCA Energy TEM 100 analytical system and a SIS MegaView II camera. Samples for analysis were suspended in methanol and placed on copper grids with a holey-carbon film support. Catalysts were analyzed before (samples reduced at 523 K, 2 h) and after being used in the glycerol steam reforming reaction. To estimate the mean particle size, the particles were considered spherical, and the second moment of the distribution was employed. The expression used for the calculation was:

$$d_{\text{TEM}} = \frac{\sum d_i n_i}{\sum n_i}$$

where *n_i* is the number of particles with *d_i* size. Over 350 particles were measured.

X-ray photoelectron spectra were acquired with a VG-Microtech Multilab 3000 spectrometer equipped with a hemispherical electron analyzer and a Mg Kα (1252 eV) 300-W X-ray source. Before recording the spectra, the samples were maintained in the analysis chamber until a residual pressure of ca. 5 × 10^{−7} N m^{−2} was reached. The spectra were collected at a pass energy of 50 eV. The intensities were estimated by calculating the integral of each peak, after subtraction of the S-shaped background, and by fitting the experimental curve to a combination of Lorentzian (30%) and Gaussian (70%) curves. All binding energies were referenced to the C 1s line at 284.6 eV. The surface Pt/Sn atomic ratios were estimated from the integrated intensities corrected by the atomic sensitivity factors. Samples were reduced “*ex-situ*” in flowing H₂ at 523 K for 2 h and conserved in octane before being analyzed by XPS.

Hydrogen chemisorption was measured in static manometric apparatus at ambient temperature. For each sample, a first hydrogen adsorption isotherm was obtained for the sample previously reduced at 523 K for 2 h and then evacuated at the same temperature overnight. After the first isotherm, the sample was evacuated at ambient temperature and a second adsorption was carried out in the same manner. The difference between the two isotherms extrapolated to zero pressure gave the quantity of the irreversibly adsorbed hydrogen, H/Pt.

2.3. Catalytic behavior

The catalytic behavior of the prepared samples in the glycerol steam reforming reaction was evaluated in mild and strong reaction conditions in a fixed-bed reactor. Prior to the activity test,

the catalysts were reduced *in situ* in a 50 mL min^{−1} H₂ flow at 523 K for 2 h. The reaction was performed in a Microactivity Reference reactor at atmospheric pressure, 623–673 K, feeding a 0.05 mL min^{−1} flow of a 10–30 wt.% glycerol in water solution and a WHSV 1.5 h^{−1}. This 10 wt.% glycerol feed composition is similar to the glycerol content obtained from the biodiesel production process after alcohol removal and acid neutralization of the glycerol fraction. Activity tests were performed using 0.200 g of catalyst diluted with SiC to avoid thermal effects. The composition of the gas stream exiting the reactor was determined by gas chromatography (Agilent Technologies), with two columns (Carboxen-1000 and Porapak-Q) and two detectors (FID and TCD). The liquid phase was analyzed by gas chromatography-mass spectrometry (GCMS-QP2010S, Shimadzu).

The catalytic performance was evaluated in terms of conversion into gaseous products (based on a carbon balance between the inlet and the outlet of the reactor), selectivity to the main reaction products (where “*i*” is CO₂, CO, CH₄ and CH_x), and hydrogen yield, which were defined as:

$$\% \text{ Conversion} = \frac{\text{C in the gas products}}{\text{C fed into reactor}} \cdot 100 \quad (1)$$

$$\% \text{ H}_2 \text{ yield} = \frac{\text{H}_2 \text{ produced experimentally}}{\text{H}_2 \text{ calculated according to Eq. (3)}} \cdot 100 \quad (2)$$

$$\text{H}_2 \text{ calculated} = 7$$

$$\cdot \left(\frac{\text{feeding} \cdot \text{density}}{\text{MW of glycerol}} \cdot \text{conc of glycerol solution} \right) \quad (3)$$

$$\% \text{ “}i\text{” selectivity} = \frac{\text{“}i\text{” produced experimentally}}{\text{C atoms in the gas products}} \cdot 100 \quad (4)$$

3. Results and discussions

3.1. Catalyst preparation and characterization

The actual Pt content of the catalysts was determined by ICP measurements as reported in Table 1, the obtained result being similar to the nominal value, within the experimental error.

Tin-modified PtSn_y catalysts were obtained in two stages. The first step took place between 363 and 423 K, and resulted in a system with organotin moieties anchored to the surface. The second step, occurring between 423 and 523 K, involved the formation of a bimetallic phase in which all the organic fragments were detached from the surface. The following equations represent the above-mentioned processes:

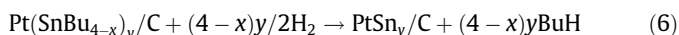


Table 1

Pt content in the catalysts, Pt dispersion and mean particle sizes of reduced and used catalysts.

Catalysts	Pt (wt.%)	<i>D</i> (%)	<i>d</i> _{TEM} (nm) ^a	<i>d</i> _{TEM} (nm) ^b
Pt/C	4.8	45	2.8	3.7
PtSn0.2/C	4.7	44	4.0	4.4
PtSn0.3/C	4.8	39	4.3	4.4
PtSn0.5/C	4.3	32	4.4	4.4
PtSn0.7/C	4.3	13	3.8	3.9

^a Reduced at 523 K.

^b After glycerol steam reforming (623 K).

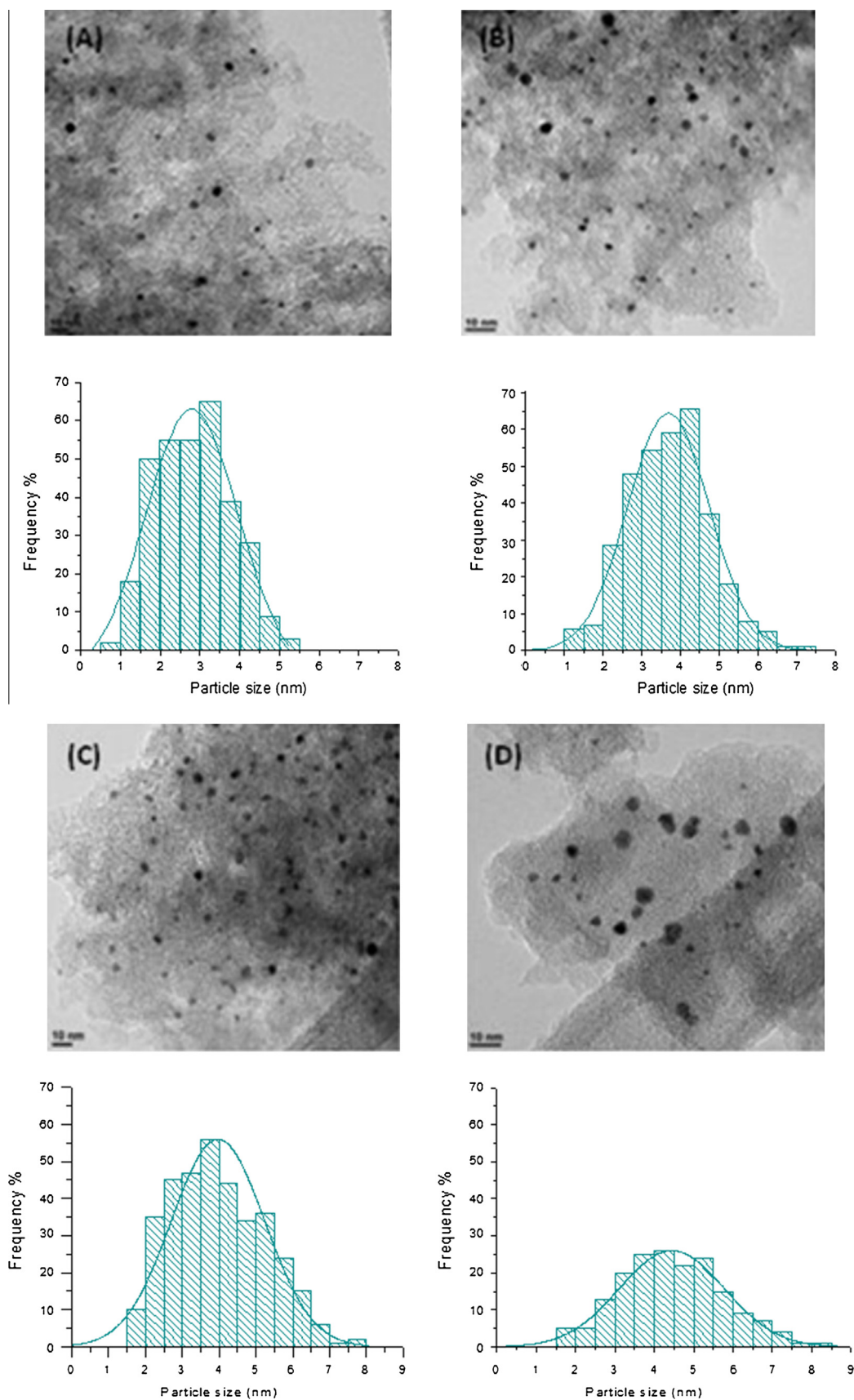


Fig. 2. TEM images (scale 10 nm) and particle size distributions for catalyst Pt/C (A and B) and PtSn_{0.2}/C (C and D) reduced at 523 K (A and C) and after glycerol steam reforming (623 K, 10 wt.% glycerol) (B and D).

The stoichiometry of the bimetallic phases, determined taking into account the actual Pt and Sn contents, was close to that expected (0.2, 0.3, 0.5 and 0.7), and it has been used to label the different bimetallic catalysts.

The results of the mean particle size obtained by TEM analysis are reported in Table 1. It can be seen that while the mean particle size in the fresh Pt/C sample is around 2.8 nm, after reaction it increased up to 3.7 nm (Fig. 2(A) and (B)). This clearly evidences the sintering of platinum particles on the carbon support. The addition of Sn produced larger particle sizes up to around 3.8–4.4 nm. This fact can be assigned in part to the selective addition of tin to the base metal. However, it is clear that this increment in particle size is somewhat larger than expected, as reported in the literature for PtSn/SiO₂ and PtSn/Al₂O₃ systems [9], and could be attributed to the thermal treatment that was carried out during the preparation process of the PtSn catalysts. On the other hand, the mean particle size (markedly in the catalysts with higher tin contents) measured after the catalysts had been submitted to the glycerol steam reforming reaction showed no appreciable changes, this indicating that Sn provided a stabilizing effect on the Pt particles, avoiding their sintering.

Fig. 2(C) and (D) shows the TEM images and particle size distributions of catalyst PtSn0.2/C, as a representative sample, before and after its use in the glycerol steam reforming reaction at 623 K. It can be seen that the metallic particles are well dispersed on the carbon support, with a homogeneous distribution of the active phase over the catalyst surface and no large agglomerations being observed.

The binding energies of Pt 4f_{7/2} and Sn 3d_{5/2} levels for the catalysts reduced in H₂ at 523 K for 2 h are reported in Table 2. For all the catalysts, the BE value corresponding to the Pt 4f_{7/2} level presented a single peak which is characteristic of platinum in the metallic state [12–15]. Contrary to previous results from studies performed with PtSn catalysts supported on SiO₂ and Al₂O₃ prepared by SOMC/M techniques [9], the Pt 4f_{7/2} peak presented only a slight shift toward lower BE (0.2 eV for the catalysts with the highest tin content, PtSn0.7/C). In Table 2 two values are given for the region corresponding to Sn 3d_{5/2}, corresponding to the deconvolution of the peak into two components. The two contributions of the Sn 3d_{5/2} peak are shown in Fig. 3. The component at a higher binding energy of ca. 486.7–486.9 eV is assigned to Sn(II, IV), and the other contribution corresponds to Sn(0), with a binding energy centered around 485.7 eV [12–16]. The presence of metallic tin in the catalysts reduced at 523 K opens up the possibility for the existence of PtSn alloy phases after this treatment, although this cannot be readily assessed by XPS. Results obtained for the Sn_{TOTAL}/Pt and Sn(0)/Sn_{TOTAL} ratios are also presented in Table 2. The values for Sn_{TOTAL}/Pt confirm that the desired amount of tin has been deposited and are consistent with previous studies that demonstrate the efficiency of the method employed to obtain these catalytic systems [10,17]. On the other hand, all the bimetallic samples have more or less the same Sn(0)/Sn_{TOTAL} ratio (Table 2). These results are thought to be responsible for the following effects: (i) dilution of platinum by metallic tin, due to the

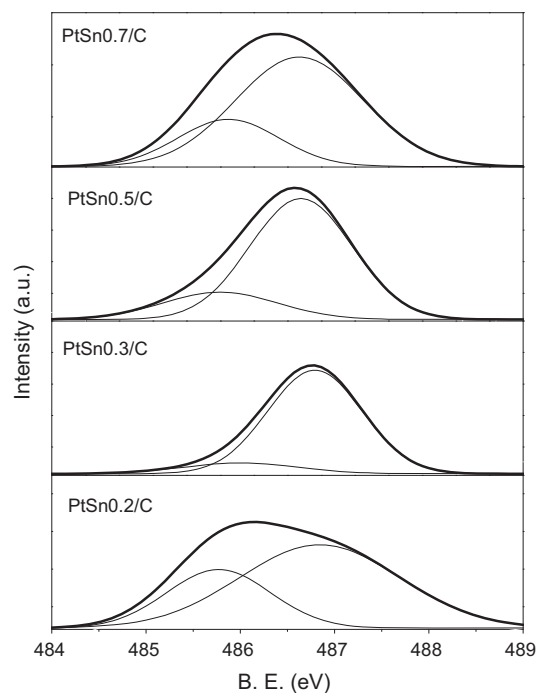


Fig. 3. XPS spectra for the Sn region (Sn 3d_{5/2} level).

formation of SnPt phases and (ii) covering of metal particles surface by oxidized tin species. Taking into account all the XPS results, the catalytic surface maybe depicted by the coexistence of SnPt phases (probably alloys), ionic tin located at the platinum–support interface and some segregated metallic platinum [12].

The Pt dispersion was determined by irreversible hydrogen adsorption on the reduced samples at room temperature, and the results are presented in Table 1. When a small amount of tin is added (catalyst PtSn0.2/C) only a slight decrease in the H₂ uptake is observed, leading to a dispersion value quite similar to that obtained for the monometallic Pt/C catalyst. Further increase in the tin content causes a decline in the amount of adsorbed hydrogen and, consequently, in the amount of surface platinum. It is well-stated that the cause of this phenomenon is the existence of simultaneous electronic and geometric effects. These effects are responsible for the decrease in adsorption energy and the destruction of adjacent Pt sites, which influence the dissociation of the H₂ molecule [9].

3.2. Glycerol steam reforming

Fig. 4 shows the results obtained in the glycerol steam reforming reaction with all the catalysts studied, Pt/C and PtSny/C, in the gas phase at 623 K, atmospheric pressure and 10 wt.% glycerol in water.

After an initial stabilization period, the conversion to gas phase compounds remained constant throughout the reaction time for all the catalysts studied. For both for the monometallic Pt/C and the bimetallic catalyst with the lowest tin content (PtSn0.2/C) a high conversion to gas phase, above 95%, was obtained. As Sn content was increased a decrease in catalytic activity was observed, this effect being more marked for the catalyst with the highest tin content, PtSn0.7/C, which achieved a conversion somewhat lower than 15%. These results can be explained considering the geometric effect of Sn on platinum: as the content of the second metal increases, more platinum active sites are blocked, thus preventing the adsorption of the glycerol molecule on the metallic surface and its subsequent reforming.

Table 2

Sn/Pt atomic ratio and binding energies (eV) of the Pt 4f_{7/2} and Sn 3d_{5/2} levels for C supported Pt and PtSn catalysts.

Catalysts	Binding energies (eV)		Sn _{TOTAL} /Pt (at/at)	Sn(0)/Sn _{TOTAL}
	Pt 4f _{7/2}	Sn 3d _{5/2}		
Pt/C	71.4	–	–	–
PtSn0.2/C	71.3	485.7–486.9	0.23	0.35
PtSn0.3/C	71.3	485.8–486.9	0.30	0.28
PtSn0.5/C	71.3	485.5–486.7	0.44	0.28
PtSn0.7/C	71.2	485.6–486.7	0.71	0.30

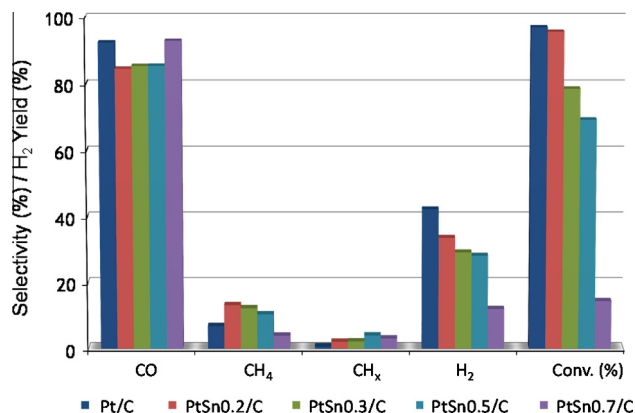


Fig. 4. H₂ yield and selectivity obtained at stable conversion (after 5 h on stream at 623 K).

The analysis of selectivity gives a clearer understanding of the various reactions taking place on the surface of the catalyst, and of the effect of Sn on the reforming reaction. In Fig. 4, selectivities to CO, CH_x and CH₄ for Pt/C and PtSn_y/C catalysts are reported. It can be seen that CO selectivity decreases as the amount of tin increases, except for catalyst PtSn0.7/C, for which the value obtained is similar to that of the monometallic catalyst. This change is accompanied by an increase in the selectivity to CH₄ and with a lower H₂ yield, which would indicate that the methanation reaction (Eq. (7)) is occurring:



The amount of CH₄ formed was quite small for all studied catalysts (CH₄/H₂ around 0.1), except for PtSn0.7/C, that generated a gas stream substantially free of this gas (CH₄/H₂ = 0.02), although CO-rich. This fact suggests that a higher Sn content somehow inhibits the methanation reaction. Similar results were obtained in the reforming of glycerol in the liquid phase using NiSn catalysts [18]. Moreover, the lower selectivity to CO cannot be attributed to the WGS reaction, since no CO₂ was detected as a reaction product.

In order to examine the effect of Sn on the stability of the catalyst, some tests were conducted using more severe reaction conditions: a feed consisting of 30 wt.% glycerol and a reaction temperature of 673 K. Catalysts with lower tin contents (PtSn0.2/C and PtSn0.3/C), which were those that showed the highest conversion and H₂ yield at 623 K and 10 wt.% glycerol, were tested,

and their catalytic behavior was compared with that of the Pt/C catalyst. As it can be seen in Fig. 5 and Table 3, similar yields to H₂ were achieved with both glycerol concentrations for the two bimetallic catalysts, despite a decrease in the conversion level with respect to the one obtained under milder reaction conditions (10 wt.% glycerol). Conversely, for the monometallic catalyst a marked decrease in the H₂ yield was observed.

Upon reaction at higher temperature (673 K) a rapid deactivation of the Pt/C catalyst was observed. However, the bimetallic systems increased the conversion level compared to that obtained at 623 K and besides, their conversion values remained relatively constant. As the temperature increases, the reactions leading to coke formation are favored. This may explain the rapid deactivation of the Pt/C catalyst that, however, showed a good stability under milder conditions. It is well-known that tin can inhibit coke formation reactions in processes such as hydrocarbon dehydrogenation [14]. Likewise, a similar effect was expected in the glycerol reforming reaction. Thus, due to electronic and/or geometric effects (which are in agreement with the results of chemisorption analysis), Sn is able to modify the catalytic properties of Pt, inhibiting reactions that produce coke precursors and thereby improving the catalysts stability. Moreover, an increase in the H₂ yield (Table 3 and Fig. 6) for the bimetallic systems was also observed.

A slight increase in the selectivity to CO₂ was observed, whereas the selectivity to CO decreased from 85% to about 79%. This variation in product distribution could be the result of the WGS reaction, which is favored with the increase of temperature and contributes to the generation of H₂. At low temperature the methanation reaction is predominant over the WGS reaction, while at higher temperatures WGS predominates [19].



Table 3
Hydrogen yield (%) obtained for different reaction conditions.

Catalysts	H ₂ yield ^a (%)		
	30% w/w of glycerol, <i>T</i> _{reaction} 623 K	10% w/w of glycerol <i>T</i> _{reaction} 623 K <i>T</i> _{reaction} 673 K	
Pt/C	19	42	2
PtSn0.2/C	32	34	36
PtSn0.3/C	23	27	36

^a 5 h reaction.

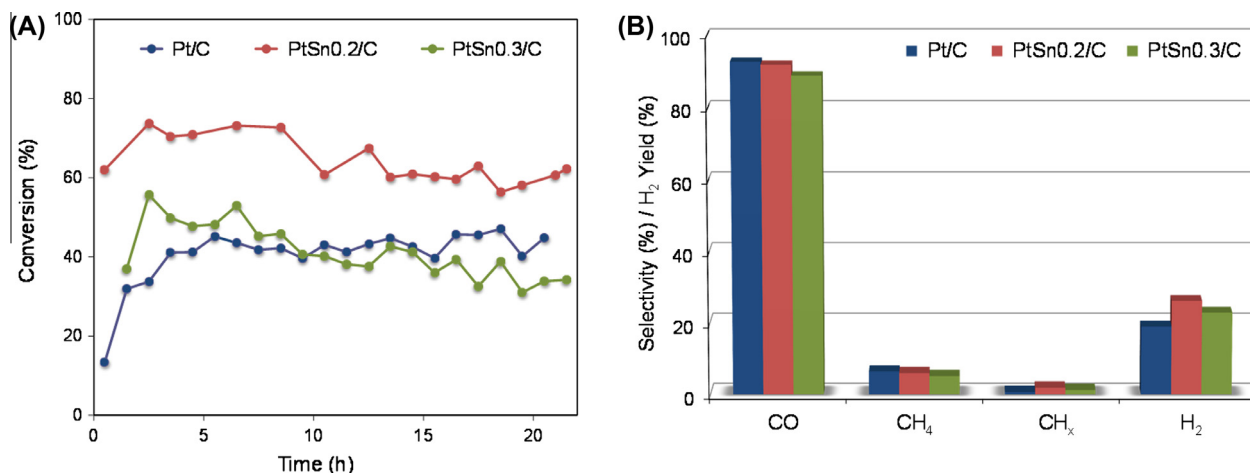


Fig. 5. Stability test for 22 h on stream at 623 K and 30 wt.% glycerol. (A) Conversion (%). (B) Selectivity and H₂ yield (%).

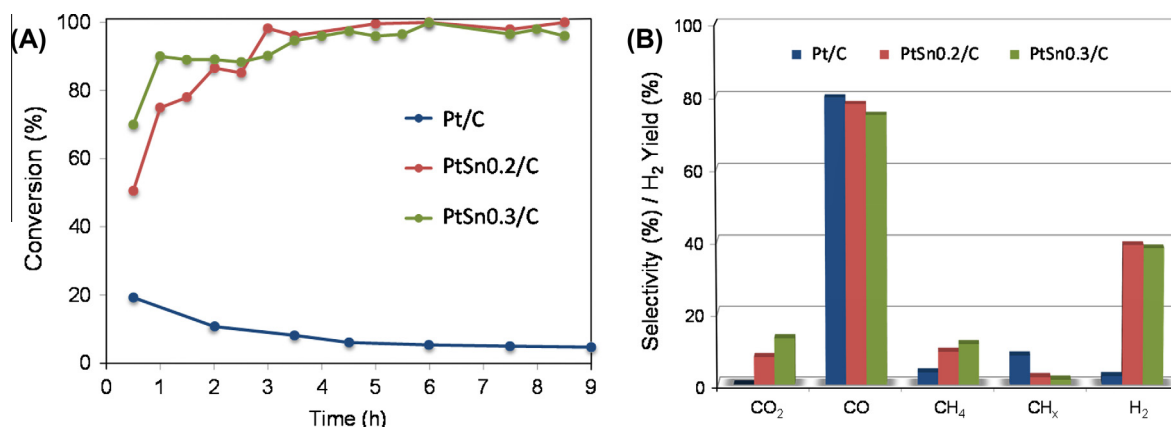


Fig. 6. Stability study of mono- and bimetallic catalysts at 673 K. (A) Conversion. (B) Selectivity and H₂ yield.

4. Conclusions

It was possible to implement techniques derived from Surface Organometallic Chemistry on Metals for the preparation of carbon-supported PtSn catalysts. TEM and XPS results highlighted the efficiency of the synthesis method used.

Bimetallic PtSn/C catalysts with low Sn/Pt ratios showed a good behavior in terms of activity and stability in the glycerol reforming reaction, both under mild reaction conditions (10 wt.% glycerol and 623 K) and under more severe conditions (30 wt.% glycerol and 673 K). At higher reaction temperature, an increase in conversion and H₂ yield were obtained with catalysts PtSn0.2/C and PtSn0.3/C, whereas the monometallic catalyst rapidly deactivated.

Acknowledgments

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