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Short Communication

Aqueous phase hydrogenolysis of glycerol to bio-propylene glycol over Pt–Sn catalysts

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ABSTRACT

PtSn supported on SiO_2 obtained via surface organometallic chemistry techniques catalyzes hydrogenolysis of glycerol to obtain bio-propylene glycol (PG). Bimetallic catalysts with Sn contents between 0.1% and 1% wt were carefully prepared by selective hydrogenolysis of $Sn(n\text{-}C_4H_9)_4$ on Pt. TEM, TPR, H_2 and CO chemisorptions, and XPS studies have shown that tin selective deposition on the metallic phase is obtained. At 200 °C under N_2 or H_2 pressure, the presence of tin increases drastically: both the selectivity and the activity of the glycerol conversion into PG. During 2 h batch runs; it could be observed that PtSn catalysts with Sn/Pt ratio = 0.2 showed the best performance (PG selectivity = 59% and 83% under N_2 and H_2 pressure respectively). The increase in activity and selectivity could be explained by the presence of Sn^{+n} species "acid Lewis sites" which would facilitate the C–OH adsorption and its subsequent C–O cleavage favoring the propylene glycol production.

1. Introduction

Nowadays, products coming from biomass arise as raw material of organic fuels and chemical products. Particularly, the glycerol availability attained as bio-diesel byproduct has inspired the study of different applications. Among these, it has been demonstrated that glycerol can be dehydrated to acrolein on acid catalysts, to hydroxyacetone on copper metallic catalysts and biopropanediols can be obtained by hydrogenolysis (Pagliaro and Rossi, 2008). From a commercial viewpoint, the production of 1,2-propanediol or propylene glycol (PG) by reduction of glycerol is the most relevant achievement of the new glycerol chemistry. Propylene glycol is an important chemical commodity traditionally derived from propylene oxide. The dependence on crude petroleum oil as a source of propylene and propylene glycol has caused instability in both price and supply, but the availability of abundant and cheap bio-glycerol can solve this problem. With the increase of the production of biodiesel, a glut of glycerol is expected in the world market and therefore, it is essential to find useful applications for bio-glycerol.

Hydrogenolysis of glycerol to PG has been previously reported to use several supported transition metal catalysts such as Ru (Alhanash et al., 2008; Wang et al., 2009), Pt (D'Hondt et al., 2008; Gandarias et al., 2010), Cu (Huang et al., 2008; Yuan et al., 2010), Ni (Perosa and Tundo, 2005) including some bimetallic catalysts consisting of Pt–Ru (Maris et al., 2007), Pt–Re (Daniel et al., 2010) Rh–Cu (Xia et al., 2012), and Ni–Cu (Gandarias et al., 2011). The activity of different supported metal catalysts for glycerol hydrogenolysis follows the order: Ru~ Cu~ Ni > Pt. The temperature had an important effect on the selectivity to propylene glycol. Dasari et al. showed that the selectivity increased until 200 °C and began to decrease as the temperature was increased further. In this way, if the temperature increased to 225 °C, the selectivity to propylene glycol decreased due to formation of alcohols such as methanol, ethylene glycol, ethanol, and gaseous products (Dasari et al., 2005). Recently, Xia et al., showed that the selectivity is kept constant in 98% in the temperature range 180–220 °C, with Rh-promoted Cu/solid-base catalyst (Xia et al., 2012).

Bimetallic Pt–Re/C catalysts (5.7 wt.% Pt, 4.6 wt.% Re) show higher activity than Pt catalyst, but lose selectivity a PG (Daniel et al., 2010). Other bimetallic systems Pt–Ru/C (1.9 wt.% Pt, 4.7 wt.% Ru) show that the selectivity improves more than the activity, compared with the Ru catalyst (Maris et al., 2007). These catalysts were prepared by incipient wetness impregnation (Pt–Re) and by surface redox reactions (Pt–Ru). These classic techniques do not assure an efficient control of the bimetallic active phase obtained. The bimetallic catalyst preparation from techniques derived from surface organometallic chemistry on metals SOMC/M is a field of chemistry devoted to the study of the reactivity of organometallic complexes with metallic surfaces (Chupin et al., 2003). It has been demonstrated that organometallic fragments can be grafted by covalent bonding directly onto the

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metallic surface of platinum particles supported on silica, which provides technical procedures to prepare catalytic systems in a controlled way (Santori et al., 2002).

It is proposed in the present work to study the reaction of hydrogenolysis of glycerol under mild operation conditions (200 °C and 16 bar N_2 or H_2 pressure) with bimetallic catalysts of Pt (1 wt.%) and Sn (0.1–1 wt%) supported on SiO_2 prepared by SOMC/M techniques.

2. Experimental

The monometallic catalyst Pt/SiO_2 was prepared by cationic exchange from a $[Pt(NH_3)_4]^{++}$ solution having such a concentration to obtain 1 wt.% Pt exchanged on the silica. The bimetallic samples (with 0.1–1 wt.% Sn) were prepared by the surface organometallic chemistry on metals route (SOMC/M). This preparation method was attached in the Supplementary data. Monometallic and bimetallic catalysts were characterized by Atomic Absorption, temperature-programmed reduction (TPR), hydrogen and CO chemisorption, X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). Experimental details were attached in the Supplementary data.

The hydrogenolysis of glycerol was carried out in a batch reactor of 100 mL with a magnetic stirrer (300 rpm). Catalysts were reduced ex situ at 500 °C for 1 h in H_2 flow. 12 mL of 10 wt.% glycerol solution and the catalyst powder were placed in the reactor; then the reactor was purged 2–3 times with N_2, and then was pressurized to 4 bar (N_2 or H_2) at room temperature and heated to the reaction temperature. At 200 °C the autogenous pressure in the reactor was 16 bar. Experimental details were attached in the Supplementary data.

3. Results and discussion

3.1. Catalyst characterization

The addition of a metal M′ (M′: Sn, Pb, Ge) from controlled techniques (SOMC/M) on supported transition metals M (M: Pt, Ru, Ni) permits to obtain bimetallic systems M′–M with well defined active phases by specific interaction between both metals, even for small values of the M′/M ratio (Chupin et al., 2003). It was demonstrated that (i) the reaction rate of $SnBu_4$, at a given temperature, does not depend on its initial concentration; (ii) an increase in temperature has a beneficial influence on $SnBu_4$ reacted. At 90 °C, it is possible to fix tin selectively onto platinum up to a Sn/Pt ratio of approximately 0.40; whereas it increases to 1.40 when the reaction temperature is 150 °C. The decomposition under H_2 flow of organometallic phases formed ($Pt_s[SnBu_x]_y/SiO_2$) occurs between 120 and 220 °C. The strong interaction of Pt and Sn of the organobimetallic phase is evidenced since $SnBu_4$ decomposes in H_2 flow at temperatures higher than 300 °C. It was verified that all butyl groups are eliminated once concluded the decomposition under H_2 flow at 500 °C (Santori et al., 2002). The reaction temperature of the preparation, the Sn content and the atomic ratio Sn/Pt are summarized in Table 1 for the different catalysts obtained. Also, results of characterization by hydrogen and CO chemisorption are included as well as mean particle size determined by TEM. Fig. 1 shows histograms of particle size distribution of some catalysts, where it was possible to note in all samples a narrow distribution of particle sizes between 1.5 and 4 nm. Table 1 indicates that the addition of small Sn amount (0.12 wt.% Sn) produced a strong decrease in the value of chemisorbed H_2 from 0.6 to 0.27. For Sn/Pt = 0.7, the H/Pt value decreased to 0.20. CO and hydrogen chemisorptions showed the similar trend. Besides, TEM results showed clearly that the Sn addition did not produce significant changes in the mean particle size (2.4–2.9 nm). This would indicate that the strong decrease of hydrogen and carbon monoxide chemisorbed is not consequence to the sintering of platinum. Authors Cortright and Dumesic determined differences in adsorption heats of H_2 and CO for Pt and PtSn, which would explain the chemisorption decrease by electronic effects (Cortright and Dumesic, 1995).

Table 1
Characterization of the catalysts studied. Amount of tin fixed at different temperatures: Sn wt.% and Sn/Pt atomic ratio. Mean particle size (d_{TEM}) by TEM and H_2 and CO chemisorption (H/Pt and CO/Pt ratios).

Catalyst	Temperature (°C)[a]	Sn wt.%	Sn/Pt	H/Pt	CO/Pt	d_{TEM} (nm)
Pt	–	0	0	0.64	0.56	2.4
PtSn0.2	90	0.12	0.2	0.27	0.29	2.7
PtSn0.4	90	0.24	0.4	0.26	0.27	2.7
PtSn0.7	120	0.42	0.7	0.20	0.25	2.9

[a] Reaction temperature between $SnBu_4$ and Pt/SiO_2.

TPR results showed two hydrogen consumption peaks in the region of 100–150 °C and 400–500 °C. With Sn addition (PtSn0.4 and PtSn0.7) there was an increase in hydrogen consumption, corresponding to the peak of low temperature ($T < 150$ °C), indicating a strong interaction between platinum and tin. TPR profiles did

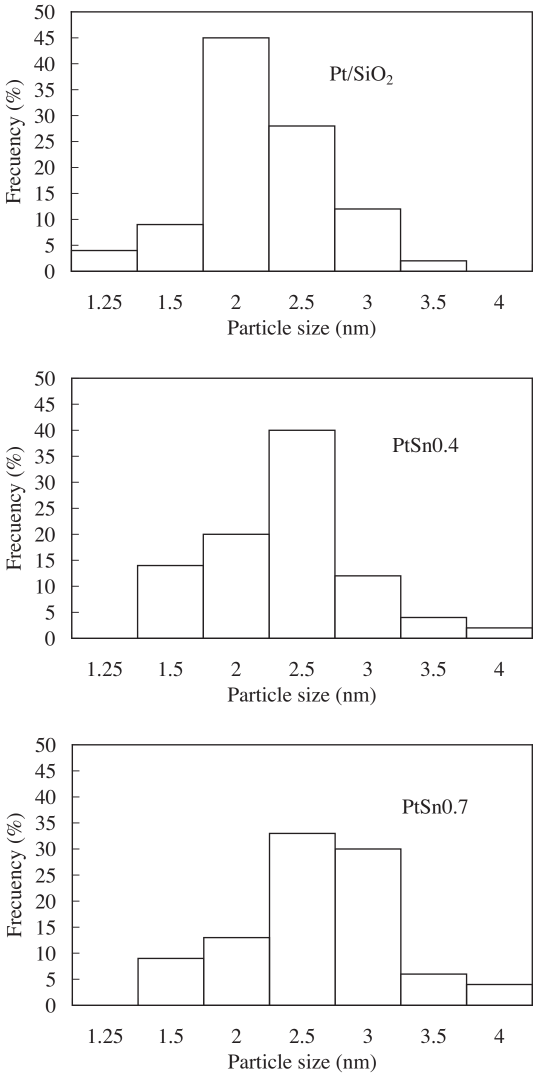

Fig. 1. Particle size distribution determined form TEM for Pt/SiO_2, PtSn0.4 and PtSn0.7 catalysts.

Table 2
Characterization by XPS. Binding energies (eV) and atomic fraction of Sn(II, IV) for PtSn catalysts.

Catalyst	Sn/Pt	Binding energies (eV)			Sn(II, IV)/ (Sn(II,IV)+ Sn(0))
		Pt $4f_{7/2}$	Sn (0) $3d_{5/2}$	Sn (II, IV) $3d_{5/2}$	
Pt	0	71.6	–	–	–
PtSn0.2	0.2	71.1	484.4	486.5	0.30
PtSn0.4	0.4	71.1	484.4	486.5	0.33
PtSn0.7	0.7	70.6	484.6	487.1	0.36

not show any peak in the zone corresponding to the reduction of bulk tin oxides, which occurs at temperatures above 630 °C.

As regards the XPS analysis, values of binding energies (BE) of levels Pt $4f_{7/2}$ and Sn $3d_{5/2}$ are reported in Table 2, referred to the binding energy of C1s of 284.6 eV. For all the studied catalysts (pre-treated in H_2 at 500 °C) in the region corresponding to Pt $4f_{7/2}$ at 71.6 eV, there appeared one peak indicating the complete reduction of platinum. Table 2 shows the XPS Sn $3d_{5/2}$ region, both Sn(II, IV) and Sn(0) were found at 486.5 and 484.4 eV respectively. The deconvolution of the spectra allowed to obtain the contribution of these species in each sample, as it is shown in the same table.

An interesting aspect arose from the analysis of the binding energy for Pt. In the three systems modified by tin, a shift was observed in the BE towards lower values of approximately 0.5–1 eV with respect to Pt/SiO_2. This change can be interpreted as an electronic transference from tin to platinum. These modifications strengthen the hypothesis of the electronic effects induced by tin which was proposed in the explanation of H_2 and CO chemisorptions. The ionic tin (Sn(II,IV)) is probably obtained by migration to the metal–support interface in which it would be present as SnOx, while Sn(0) would form PtSn superficial alloys. The fraction of Sn(0) decreased slightly from 70 to 64% as Sn/Pt increases from 0.2 to 0.70.

3.2. Hydrogenolysis of glycerol

Table 3 shows the results of hydrogenolysis of glycerol on different catalysts studied, under initial N_2 or H_2 pressure. Pt catalyst showed that at temperatures lower than 200 °C the catalytic activity was negligible, while at temperatures higher than 225 °C, undesirable C–C cleavage reactions resulted favored. The PtSn bimetallic catalysts showed a marked activity increase with respect to the Pt catalyst. In the activity test performed at 200 °C, the main reaction products identified were propylene glycol > acetol > ethylene glycol > methanol∼ethanol∼1-propanol. On the order hand, the conversion to gases was very low, 1% for the monometallic catalyst and between 3% and 5% for the bimetallic catalysts, which indicates a very low contribution of C–C cleavage reactions of APR of glycerol. The composition of gaseous products was 71% H_2, 1% CH_4 and 28% CO_2 for the test performed under N_2 pressure with Pt catalyst, and approximately 25% H_2, 1% CH_4 and 74% CO_2 with PtSn catalysts. Due to the increased activity of Pt–Sn catalysts, H_2 is consumed to hydrogenate the main intermediary (acetol) a PG. It can be observed in Table 3 that the initial H_2 pressure would inhibit the first step of glycerol dehydrogenation; this would explain the lower activity and the higher selectivity a PG compared with initial N_2 pressure.

For the experiment under N_2 pressure, the PtSn0.2 catalyst showed 55% of X_{GLY} with 59% selectivity to propylene glycol leading to the highest yield to propylene glycol (Y_{PG} = 32%). When the Sn/Pt ratio increased to 0.4, the activity was similar (the X_{GLY} is 50% and the selectivity is 63%). For Sn/Pt ratio equal to 0.7, the activity decreased (X_{GLY} = 36%) and the Y_{PG} was reduced to 22%. It can be observed that for Sn/Pt ratio from 0.2 to 0.7, the decrease in activity was similar to the reduction of surface platinum sites determined by H_2 chemisorption.

In bimetallic systems it is accepted a number of adjacent site; or an ensemble of several atoms is required for the hydrogenolysis (Asedegbega-Nieto et al., 2006). PtSn bimetallic catalysts would have this number of adjacent site of Pt–Sn for Sn/Pt ratio between 0.2 and 0.7. As it was observed by XPS, the tin, apart from being found as Sn(0), presents an important contribution of ionic tin (Sn II, IV), which would favor the polarization of the C–OH bond. The carbon atom polarized positively is bound to a Pt atom whose electronic density would result increased by the Sn addition. On the other hand, the oxygen atom of the C–OH group is bound to an ionic tin that acts as "Lewis acid sites". This fact would produce a weakening of the C–OH bond, allowing the C–O cleavage to obtain acetol. Besides, the PtSn bimetallic system preserved the capacity to chemisorb and dissociate H_2 to convert the acetol into propylene glycol. This mechanism could explain that even when the contribution of APR of glycerol is low, hydrogenolysis reaction is possible. Other authors (Gandarias et al., 2010) suggest that support acid sites and Pt site are involved on glycerol dehydration to acetol, and that the hydrogenation takes place due to the H_2 available from the APR of glycerol at 220 °C. In the same way, Roy et al., explain the lower activity of Ru due to the fact that it is not a very good catalyst for reforming and as such, there was insufficient hydrogen generated in situ to convert the remaining glycerol to PG (Roy et al., 2010).

Finally, for PtSn with 1 wt.% Sn (Sn/Pt = 1.4 ratio), the catalyst was inactive with respect to hydrogenolysis reaction. This evidenced the need to use a controlled preparation method for the

Table 3
Results of glycerol hydrogenolysis over Pt and PtSn catalysts.

Catalyst	Pt			PtSn0.2		PtSn0.4		PtSn0.7
	N_2	N_2[a]	H_2	N_2	H_2	N_2	H_2	N_2
Conversion to liquid products X_{GLY} (%)	1	3	0.6	54	16	49	6	35
Reaction rate[b]	15	16	7.5	907	272	842	264	795
Selectivity to liquid products (% mol/mol)								
Methanol	6	15	11	1	1	1	1	1
Ethanol	11	7	10	2	2	1	1	1
1-Propanol	1	1	–	2	2	1	1	0
Acetol	32	16	23	25	3	27	5	32
Ethylene glycol	–	19	–	11	8	7	10	4
Propylene glycol	50	42	56	59	84	63	82	62
Yield Y_{PG} (%)[c]	0.4	4.8	0.3	32	13	31	12	22

Reaction condition: P initial = 4 bar, T: 200 °C, reaction time: 2 h, 10 wt.% glycerol solution, catalyst mass: 300 mg.

[a] P initial = 4 bar, T = 225 °C, reaction time: 2 h, 10 wt.% glycerol solution, catalyst mass: 500 mg, Gaseous conversion: 10%.

[b] Reaction rate: [mol × (mol of Pt exposed)$^{-1}$ h^{-1}].

[c] Y_{PG} = [(produced moles of propylene-glycol) × (initial moles of glycerol)$^{-1}$] × 100.

bimetallic catalyst in order to achieve low Sn/Pt ratios with strong interaction between Pt–Sn and the presence of ionic tin (Sn (II, IV)) so as to promote C–O cleavage versus C–C cleavage reactions.

4. Conclusions

It was demonstrated in this work that the addition of Sn (between 0.12 and 0.42 wt.%) by surface organometallic route on a platinum surface can strongly modify the activity and selectivity of the hydrogenolysis of glycerol to obtain bio-propylene glycol. The highest yield is obtained with the catalyst PtSn0.2. For higher tin contents, the decrease in the activity is related to the reduction of accessible platinum sites. The ionic tin presence acting as "Lewis acid sites" and the platinum with higher electronic density lead to a favorable site for the adsorption of the C–OH group and subsequent C–O cleavage, initial step in the production of propylene glycol.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.biortech.2012.02.053.

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