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Use of Al_2O_3–SnO_2 as a support of Pt for selective dehydrogenation of light paraffins

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Abstract

The influence of the preparation methods of Al_2O_3–SnO_2 on the catalytic behaviour of Pt supported on the above supports in the *n*-butane dehydrogenation reaction was studied. Two methods were used for the preparation of the support with different Sn loadings: (i) incipient impregnation and (ii) impregnation with an excess of solution. It was determined that the second preparation method would lead to more homogeneous catalysts than the incipient impregnation with $SnCl_2$. Different characterization techniques (XPS, TPR, SEM, test reactions of the acidic and metallic functions, H_2 chemisorption) showed that geometric effects and also possible electronic effects between Pt and Sn with probable alloys formation could take place in Pt/Al_2O_3–SnO_2 catalysts. In all cases it was found an excellent behaviour in the *n*-butane dehydrogenation even when higher Sn contents in the support were used.

Keywords: Metallic catalysts for *n*-butane dehydrogenation; Al_2O_3–SnO_2 support; Catalyst preparation; Catalyst characterization

1. Introduction

The production of light molecular weight olefins, such as butenes (1-butene, *cis*- and *trans*-2-butene, and butadiene) from *n*-butane, is a process with high industrial interest [1]. The catalysts should give a high yield to butenes, with a minimum catalyst deactivation and a high catalytic stability. Bimetallic catalysts supported on alumina are active for dehydrogenation of low and high molecular weight paraffins [2–4]. In the case of the dehydrogenation catalysts, the side reactions (cracking, isomerization and polymerization), which are catalyzed by acid centers, should be inhibited in order to increase the yield to the corresponding olefins. One way to minimize the undesirable side reactions is to poison the acid sites of the support by the addition of alkali metal ions during the preparation of the catalysts. It must be indicated that several studies on this topic have been reported in the literature. Thus, Pines and Haag [5] found that alkali metal ions poison the Lewis acid sites of the alumina. Jiratová and Beránek [6] reported a selective poisoning of the support when alumina is doped with Na ions. García Cortéz et al. [7], by using ammonia thermodesorption, found that Li, Na and K ions poison the acid sites of alumina. Moreover, these authors reported that the strong acid sites are poisoned by the addition of small quantities of alkali metal ions. Further addition of these ion blocks centers with lower acid strength. Likewise, they also found that the toxicity of the alkali metals on the acid character of alumina increases with the ionic radius, though the poisoning effect of Na, K and Li would not be related only to a steric effect. Besides, de Miguel et al. [8] found, through FTIR of pre-adsorbed CO and NMR measurements, that K and Li addition poisons mainly the OH configuration of type Ia (OH group bonded to tetrahedral Al^{3+}, according to the model of the alumina surface proposed by Knözinger and Ratnasamy [9]), this effect being more pronounced for K. However, the addition of alkali metals to alumina not only modifies the acid function, but it could also affect the structure of the metallic phase. In fact, Mross [10] reported that the alkali metals could change the electronic structure of the transition metals, and in consequence, the activity in the CO hydrogenation

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reaction would be enhanced. Park and Price [11,12] reported that the K addition to the Pd/Al_2O_3 catalyst increases both the activity and the selectivity in the acetylene hydrogenation. This behaviour was explained in terms of the increase of the support basicity, followed by an electronic transference from K to Pd.

The literature about PtSn supported on pure and doped aluminas [2–8], and other inert supports [13–16] is wide, but the use of the Al_2O_3–SnO_2 as a support of Pt has been scarcely reported in the literature [17]. This paper reports the behaviour of Pt/Al_2O_3–SnO_2 prepared by different methods in the selective dehydrogenation of *n*-butane. The supports and catalysts were characterized by different techniques, such as SEM, TPR, test reaction of the acidic function (isopropanol dehydration), test reactions of the metallic phase (cyclohexane dehydrogenation and cyclopentane hydrogenolysis), H_2 chemisorption, TPR, and *n*-butane dehydrogenation in flow and pulse equipments.

2. Experimental

2.1. Preparation of the Al_2O_3–SnO_2 supports

The Sn composition of the supports used in this paper were 0.8, 2.5 and 5 wt%. Tin was added to Al_2O_3 (CK 300 from Cianamyd Ketjen) by two ways: impregnation with excess of aqueous solution (IES) and incipient impregnation (II) procedure by using a solution of $SnCl_2 \cdot 2H_2O$ (from Carlo Erba, 98% purity). In the case of the II, the volumetric ratio between the tin solution and the alumina weight was 1 mL g^{-1}. In the case of IES, the above-mentioned ratio was 20 mL g^{-1}. In both cases the impregnations were carried out at 25 °C for 6 h. In the case of IES, the solid was separated from the liquid by filtration and the Sn content in the solid was determined. After impregnation, the samples were dried at 110 °C for 12 h, and then they were calcined in air at 400 °C for 3 h (in both cases).

2.2. Preparation of Pt/Al_2O_3–SnO_2 catalysts

Pt (0.3 wt%) was deposited on the different Al_2O_3–SnO_2 supports by impregnation. In fact, the supports were impregnated with an aqueous solution of H_2PtCl_6 (Aldrich 99%) by using an impregnating solution volume/weight of support of 1.4 mL g^{-1} for 6 h at room temperature. Then the samples were dried at 110 °C overnight and finally calcined in flowing air at 400 °C for 3 h.

Besides, a sample of Al_2O_3–SnO_2 (5 wt% Sn) was impregnated with a hydrochloric solution (2N) of the bimetallic complex $(Me_4N)_2[PtCl_2(SnCl_3)_2]$. The Pt content in this sample was 0.3 wt% and it was called as PtSn complex/Al_2O_3–SnO_2 (5 wt% Sn). The complex was synthesized following the technique reported in the literature [18]. In this way H_2PtCl_6 and $SnCl_2$ solutions were mixed in hydrochloric medium (2N) with the following stoichiometric ratio: Pt(IV)/Sn(II) = 1/2. Then tetramethylammonium chloride (Me_4NCl, Merck 99%) was added to this bimetallic solution in the stoichiometric amounts, thus obtaining the PtSn complex as a red-orange precipitate, which was filtered and washed with water. The synthesis yield was 65%.

2.3. Characterization of the supports and the metallic phase

The specific surface area of the supports prepared by different procedures was determined with a Micromeritics ASAP 2000 equipment by using N_2 at $-196°$ C. Before S_{BET} measurements, samples were treated at 200 °C under high vacuum (10^{-4} Torr) for 2 h.

SEM microphotographies were obtained in a Microscope Jeol JSM-35C, operated at 2 kV, equipped with an acquisition system of digital images SemAfore. Samples were covered with a gold film (deposited by sputtering with a vaporizator VEECO, model VE-300, operated in Ar atmosphere) before the analysis. The measurements were carried out under the mode of secondary electrons image, using 20 kV as acceleration voltage.

The samples of Al_2O_3–SnO_2 were evaluated in the isopropanol dehydration reaction at 1 atm. in a flow reactor in order to determine the modification of the acid sites. The alcohol was evaporated in a H_2 flow (600 mL min^{-1}) and fed to the reactor with the space velocity of 0.52 mol alcohol h^{-1} g^{-1}. The catalysts were previously reduced under flowing H_2 at 500 °C for 3 h. The catalyst weight was 0.15 g, the reaction temperature was 225 °C. Reaction products were analyzed by gas chromatography with a FID detector.

The metallic phase was characterized by test reactions (cyclohexane (CH) dehydrogenation and cyclopentane (CP) hydrogenolysis). These reactions were carried out in a differential flow reactor with H_2/CH and H_2/CP molar ratios of 26 and 22, respectively. The reaction temperature was 450 °C for the first reaction and 500 °C for the second one. The reaction products were analyzed by gas chromatography with a FID detector. Besides, temperature-programmed reduction (TPR) experiments were carried out in a quartz flow reactor. The samples were heated at 6 °C min^{-1} from room temperature up to 750 °C. The reductive mixture (5% (v/v) H_2/N_2) was fed to the reactor with the flow rate of 10 mL min^{-1}. Catalysts were previously calcined in situ at 500 °C for 3 h. Hydrogen chemisorption measurements were made in a volumetric equipment. The sample was heating under flowing H_2 (60 mL min^{-1}) from room temperature up to 500 °C and kept at this temperature for 3 h. Then, the sample was outgassed under vacuum (10^{-4} Torr) for 1 h. After the sample was cooled down to room temperature (25 °C) the dosage was performed in the range 50–250 Torr.

XPS measurements were carried out in a VG—Microtech Multilab spectrometer, which operates with an energy power of 50 eV (radiation Mg Kα, $h\nu = 1253.6$ eV). The pressure of the analysis chamber was kept at 4×10^{-10} Torr. Samples were previously reduced at 500 °C for 2 h. Binding energies (B.E.) were referred to the C1s peak at 284.9 eV. The peak areas were estimated by fitting the experimental results with Lorentzian–Gaussian curves.

2.4. Evaluation of the catalytic performance in n-butane dehydrogenation

Two different *n*-butane dehydrogenation tests were carried out, one of them in a continuous flow reactor and another in a pulse equipment. The continuous flow experiment was performed at 530 °C for 2 h in a quartz flow reactor heated by an electric furnace. The reactor (with a catalyst weight of 0.200 g) was fed with 18 mL min^{-1} of the reactive mixture (*n*-butane + hydrogen, $H_2/n\text{-}C_4H_{10}$ molar ratio = 1.25). The reactive mixture was prepared ‘‘in situ’’ by using mass flow controllers. All gases, *n*-butane, N_2 (used for purge), and H_2 (used for the previous reduction of catalysts and for the reaction) were high purity ones (>99.99%). Prior to the reaction, catalysts were reduced ‘‘in situ’’ at 803 K under flowing H_2 for 3 h. The reactor effluent was analysed in a GC-FID equipment with a packed chromatographic column (1/8 in. × 6 m, 20% BMEA on Chromosorb P-AW 60/80), which was kept at 323 K during the analysis. With this analytical device, the amounts of methane, ethane, ethylene, propane, propylene, *n*-butane, 1-butene, *cis*-2-butene, *trans*-2-butene and 1,3-butadiene were measured. The *n*-butane conversion was calculated as the sum of the percentages of the chromatographic areas of all the reaction products (except H_2) corrected by the corresponding response factor. The selectivity to the different reaction products (i) was defined as the ratio: mol of product $i/\sum$ mole of all products (except H_2). Taking into account the high temperatures used for the reaction (for thermodynamic reasons), it was necessary to determine the contribution of the homogeneous reaction. For this purpose, a blank experiment was performed by using a quartz bed and the results showed a negligible *n*-butane conversion ($\ll 1\%$).

The pulse experiments were performed by injecting pulses of pure *n*-butane (0.5 mL STP) into the catalytic bed (0.100 g of sample) at 530 °C. The catalytic bed was kept under flowing He (30 mL min^{-1}) between the injections of two successive pulses. Prior to the experiments, all samples were reduced ‘‘in situ’’ under flowing H_2 at 530 °C for 3 h. The composition of each pulse after the reaction was determined by using a GC-FID equipment with a packed column (Porapack Q). The temperature of the chromatographic column was 30 °C. In these experiments the *n*-butane conversion was calculated as the difference between the chromatographic area of *n*-butane fed to the reactor and the chromatographic area of non-reacted *n*-butane at the outlet of the reactor, and this difference was referred to the chromatographic area of *n*-butane fed to the reactor. The selectivity to a given product was calculated in the same way than for flow experiments. The carbon amount retained on the catalyst after the injection of each pulse was calculated through a mass balance between the total carbon amount fed to the reactor and the total carbon amount detected by the chromatographic analysis at the outlet of the reactor. The accumulative carbon retention was calculated through a carbon mass balance and expressed as the sum of the carbon amount retained after each pulse.

3. Results and discussion

Table 1 shows the physical properties of the $Al_2O_3–SnO_2$ supports prepared both by incipient impregnation (II) and impregnation with excess solution (IES) and with increasing amounts of tin contents (0.8, 1.5, 2.5, 3.5 and 5 wt%). Both the specific surface areas and the porosity are similar to those of the γ-Al_2O_3 and are practically not modified by using both methods of tin introduction and different tin contents (up to 5%).

In order to study the better way of tin impregnation on the γ-Al_2O_3, two methods were compared: incipient impregnation (II) and impregnation with excess of solution (IES). In the case of II, there was not a separation of the liquid after Sn deposition. The results of Sn content obtained by chemical analysis were the same than the nominal values (±3%) for all the Sn loadings. It must be remembered that in the case of impregnation of Sn over Al_2O_3 using the IES method, the solid was separated from the liquid after the impregnation and submitted to chemical analysis. Fig. 1 shows the amounts of Sn deposited on the solid as a function of the nominal Sn content initially added. It can be observed that there is a strong and total adsorption of Sn in all range of Sn loadings. Hence, this preparation method is effective for the Sn deposition in a wide range of Sn loading up to 8 wt%.

Moreover, the $Al_2O_3–SnO_2$ supports prepared by IES were evaluated in the reaction of isopropanol dehydration in order to study the influence of tin on the acidity of Al_2O_3. Table 2 shows the results of dehydration activity and selectivity to propylene and di-isopropylether. This Table shows a decrease of the dehydration activity with the Sn content, thus indicating that the acidic sites of the alumina are poisoned by the addition of increasing amounts of tin. Besides, a change in the selectivity to products is observed. This behaviour can be related to the modification of the distribution of the acid sites with different

Table 1
Values of BET surface and porosity for catalysts prepared by the different methods

Catalyst	II		IES	
	BET surface (m^2/g)	Porosity (mL/g)	BET Surface (m^2/g)	Porosity (mL/g)
$Al_2O_3–SnO_2$ (0.8%)	189	0.40	197	0.50
$Al_2O_3–SnO_2$ (1.5%)	191	0.48	187	0.46
$Al_2O_3–SnO_2$ (2.5%)	191	0.48	196	0.45
$Al_2O_3–SnO_2$ (3.5%)	183	0.48	189	0.42
$Al_2O_3–SnO_2$ (5%)	180	0.44	196	0.48

II: incipient impregnation; IES: impregnation with excess of solution.

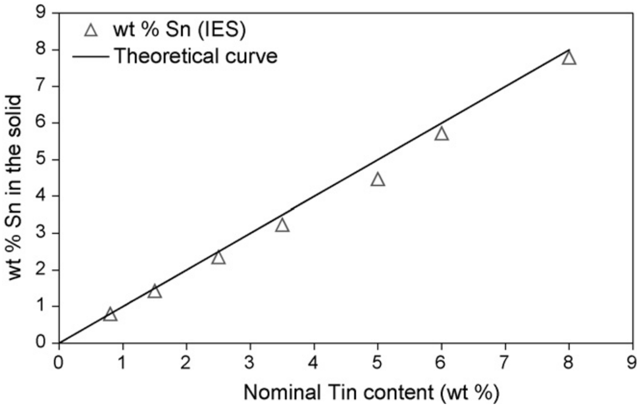

Fig. 1. Amounts of deposited Sn on γ-Al_2O_3 vs. nominal Sn content, using the method of impregnation with excess of solution (IES) for Al_2O_3–SnO_2 samples.

acid strength when tin loading is increased. These results are in agreement with those reported by Passos et al. [19], who found IR of adsorbed pyridine that the amount of Lewis acid sites of Al_2O_3 (band at 1453 cm^{-1}) decreased after tin addition.

Fig. 2(a)–(c) shows the SEM images corresponding to calcined alumina, Al_2O_3–SnO_2 (5 wt% of Sn) prepared by II and Al_2O_3–SnO_2 (5 wt% of Sn) prepared by IES, respectively. It can be observed that Sn is deposited on the support surface in a different way according to the impregnation method, in comparison with calcined alumina used as a reference. Besides, according to EDX measurements on different zones of the samples and the SEM images, it can be observed a higher homogeneity in the tin distribution in samples prepared by IES than in samples prepared by II.

In order to study the catalytic performance of Pt catalysts supported on Al_2O_3–SnO_2 prepared by II and Al_2O_3–SnO_2 prepared by IES, reaction experiments in *n*-butane dehydrogenation in flow reactor were carried out. Fig. 3(a) and (b) shows the change of the conversion with reaction time for the catalysts containing different Sn loadings. Pt catalyst supported on Al_2O_3–SnO_2 (2.5 and 5 wt% Sn) prepared both by II and IES show similar catalytic behaviors: high initial activity and very low deactivation along the reaction time. On the other hand, Pt/Al_2O_3–SnO_2 (0.8 wt%) prepared by II displays an important activity loss with respect to the partner prepared by IES, which shows a good catalytic stability. In this way, the catalyst with the lowest tin content prepared by II, due to its higher heterogeneity in the tin distribution, would tend to the catalytic behavior of the Pt/Al_2O_3 sample (shown in Fig. 3(a) as a reference). The selectivities to butenes for the Pt/Al_2O_3–SnO_2 (2.5 and 5 wt%) catalysts prepared both by II and IES reached similar final values (89–92%), while the final selectivities for the Pt/Al_2O_3–SnO_2 (0.8 wt%) catalysts, prepared by II and IES, were about 85%. From the above-mentioned results it is clear that Al_2O_3–SnO_2 prepared by IES as a support of Pt leads to a

Table 2
Values of isopropanol (IPA) conversion and selectivities (SP: selectivity to propylene, SDIE: selectivity to di-isopropylether) of Al_2O_3–SnO_2 catalysts

Catalyst	IPA conversion (%)	SP (%)	SDIE (%)
Al_2O_3–SnO_2 (0.8% Sn)	19.0	88	12
Al_2O_3–SnO_2 (1.5% Sn)	17.5	85	15
Al_2O_3–SnO_2 (2.5% Sn)	11.0	83	17
Al_2O_3–SnO_2 (3.5% Sn)	6.5	74	26
Al_2O_3–SnO_2 (5% Sn)	<1	–	–

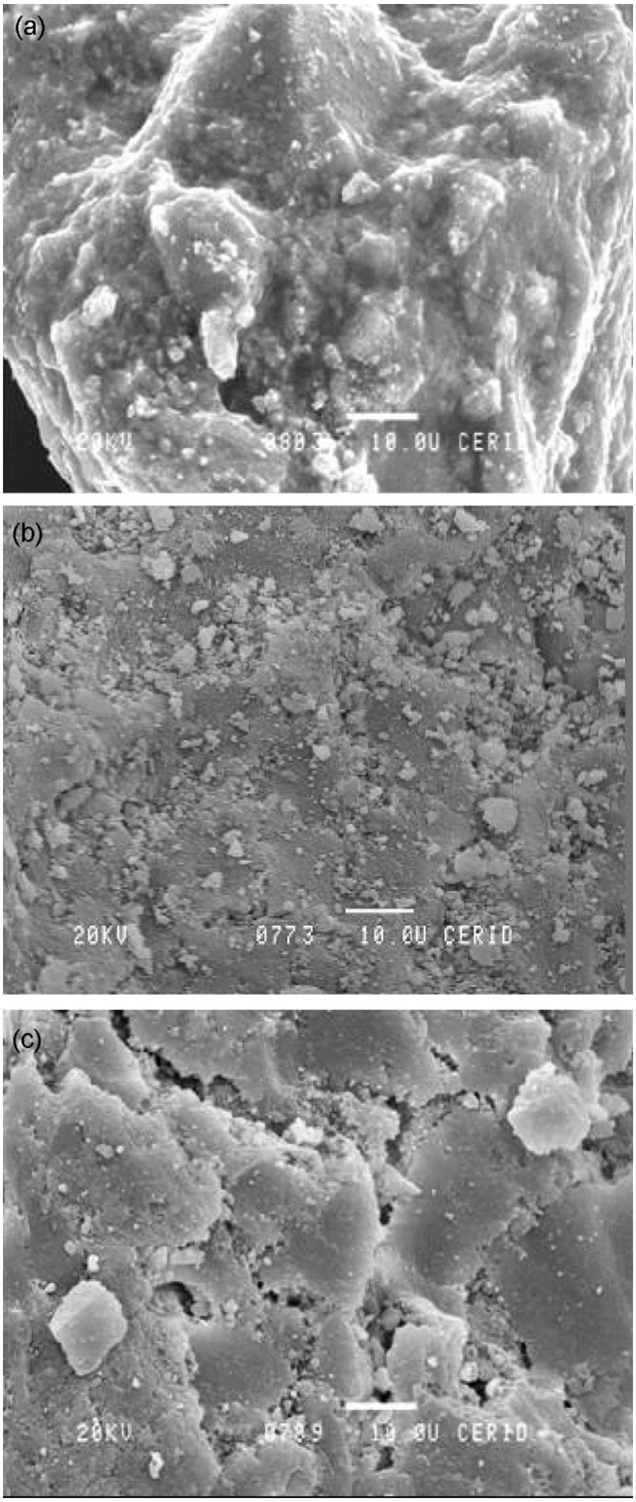

Fig. 2. SEM microphotographies: (a) calcined γ-Al_2O_3, (b) Al_2O_3–SnO_2 (5 wt%) prepared by II and (c) Al_2O_3–SnO_2 (5 wt%) prepared by IES.

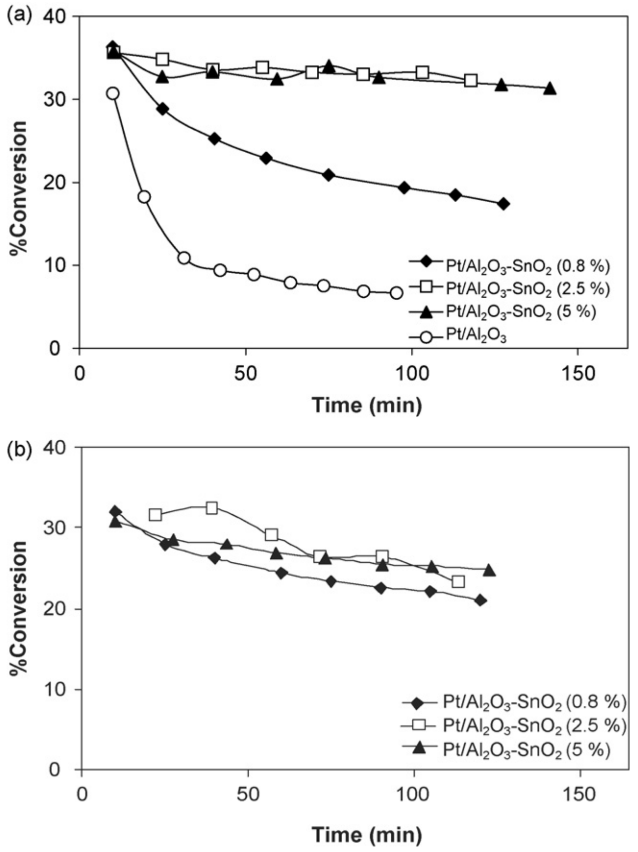

Fig. 3. Conversion of *n*-butane vs. reaction time for Pt(0.3 wt%)/Al_2O_3–SnO_2 catalysts (with different tin contents) prepared by (a) impregnation of Sn by II and (b) impregnation of Sn by IES.

better catalytic performance than the Al_2O_3–SnO_2 prepared by II.

Hence, taking into account the above-mentioned results, all studies will be performed only on catalysts supported on Al_2O_3–SnO_2 prepared by IES with different tin contents.

Table 3 shows the results of cyclohexane dehydrogenation (initial reaction rate (R_{CH}) and activation energy (E_{CH})) and cyclopentane hydrogenolysis (initial reaction rate (R_{CP})). It is observed for cyclohexane dehydrogenation (structure-insensitive reaction) that Pt catalysts supported on Al_2O_3–SnO_2 display a decrease of the activity and an increase of the E_{CH} when the Sn content in the catalysts is increased. Taking into account the insensitive-character of this reaction [20], the increment of E_{CH} with the Sn content would indicate an electronic modification of the nature of the active phase with probable alloy formation. It must be noted that the complex deposited on AlO_3–SnO_2 displays the lowest activity and the highest activation energy, thus indicating a higher electronic interaction in this catalyst.

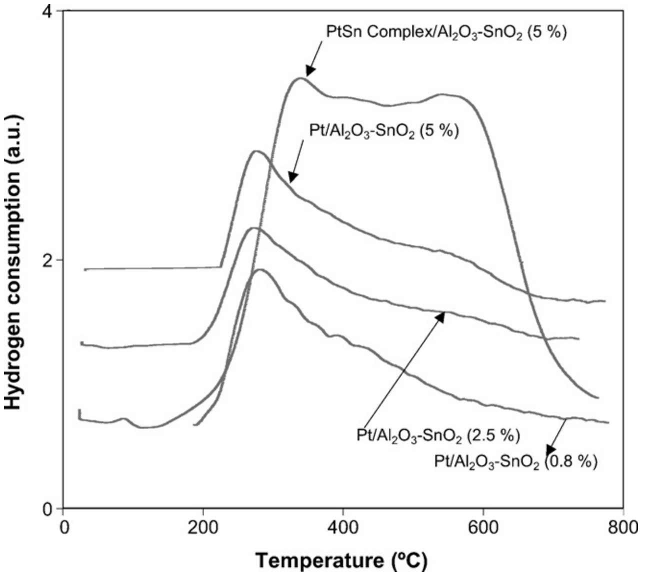

Fig. 4. TPR profiles of Pt and PtSn complex supported on Al_2O_3–SnO_2 (IES).

In the cyclopentane hydrogenolysis reaction (structure-sensitive reaction [21]), it is observed a negligible activity for catalysts with tin contents of 2.5 and 5 wt%, and a very low activity for catalysts with 0.8 wt% Sn. This fact would indicate than Pt is geometrically modified by the tin addition, thus causing a pronounced decrease in the concentration of the metallic ensembles needed for the hydrogenolysis.

Fig. 4 shows the temperature-programmed reduction (TPR) profiles for the different catalysts. It is observed for Pt/Al_2O_3–SnO_2 (0.8, 2.5 and 5 wt% Sn) prepared by IES, the presence of a defined zone of H_2 consumption at low temperatures (about 250 °C), due probably to a co-reduction of Pt and Sn species or to Pt–Sn interactions. For the samples with higher tin contents, it can be also observed an additional zone of H_2 consumption at high temperatures (about 600 °C), which could be related to the reduction of free Sn species [22]. With reference to the catalyst prepared with the PtSn complex, it can be observed a reduction zone at temperatures about 400 °C, probably due to the Pt–Sn

Table 3
Values of initial reaction rates (R_{CH}) and activation energy (E_{CH}) in cyclohexane (CH) dehydrogenation and initial rates (R_{CP}) in cyclopentane (CP) hydrogenolysis, for different catalysts

Catalyst	CH dehydrogenation reaction at 450 °C		CP hydrogenolysis reaction at 500 °C
	R_{CH} (mol/h g Pt)	E_{CH} (kcal/mol)	R_{CP} (mol/h g Pt)
Pt(0.3%)/Al_2O_3–SnO_2 (0.8%)	259.9	6.35	6.08
Pt(0.3%)/Al_2O_3–SnO_2 (2.5%)	99.47	8.32	n.d.
Pt(0.3%)/Al_2O_3–SnO_2 (5%)	12.01	27.9	n.d.
PtSn complex/Al_2O_3–SnO_2 (5%)	3.54	30.4	n.d.

n.d.: not detected.

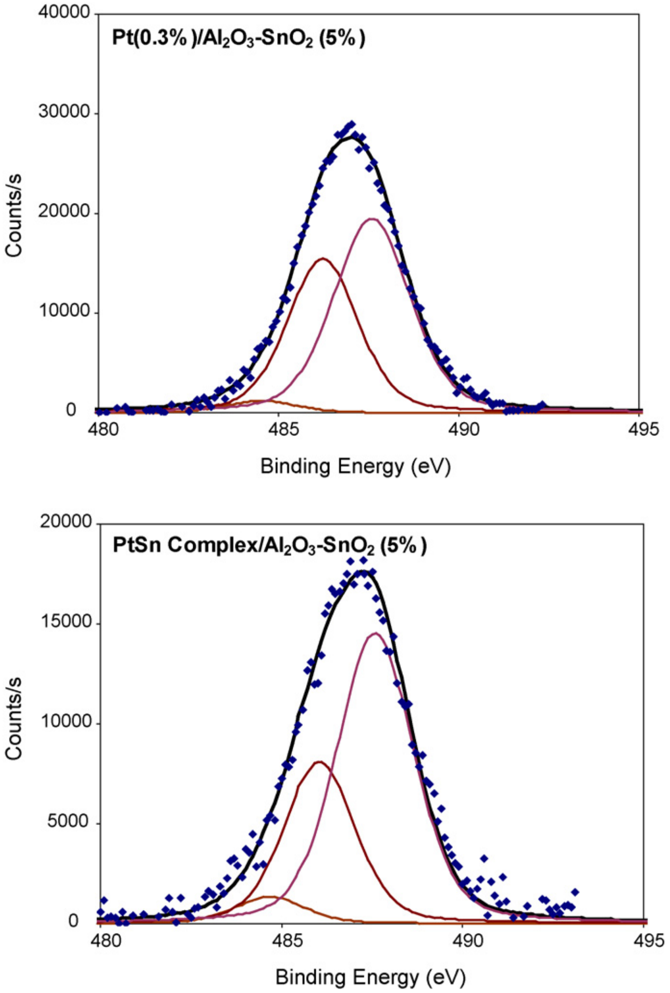

Fig. 5. XPS spectra corresponding to the Sn 3d5/2 level for Pt and PtSn complex supported on Al_2O_3–SnO_2 (IES).

interactions, and the second reduction zone displays a maximum at 600 °C which can be attributed to the reduction of free Sn species.

The hydrogen chemisorption values (total (HT), and irreversible (HI)) for the metallic catalysts supported on Al_2O_3–SnO_2 prepared by IES and the sample prepared from the PtSn complex are reported in Table 4. It can be observed in Table 4, that when the tin content increases the chemisorption capacity decreases. This behaviour can be related to the presence of an electronic modification of the metallic phase. This effect is more pronounced for the sample impregnated with the PtSn complex.

Table 4
Values of total and irreversible H_2 chemisorption for different catalysts

Catalyst	H_2 (total) (μmol/g)	H_2 (irreversible) (μmol/g)
Pt(0.3%)/Al_2O_3–SnO_2 (0.8%)	8.22	7.66
Pt(0.3%)/Al_2O_3–SnO_2 (5%)	7.74	6.44
PtSn Complex/Al_2O_3–SnO_2 (5%)	6.30	5.20

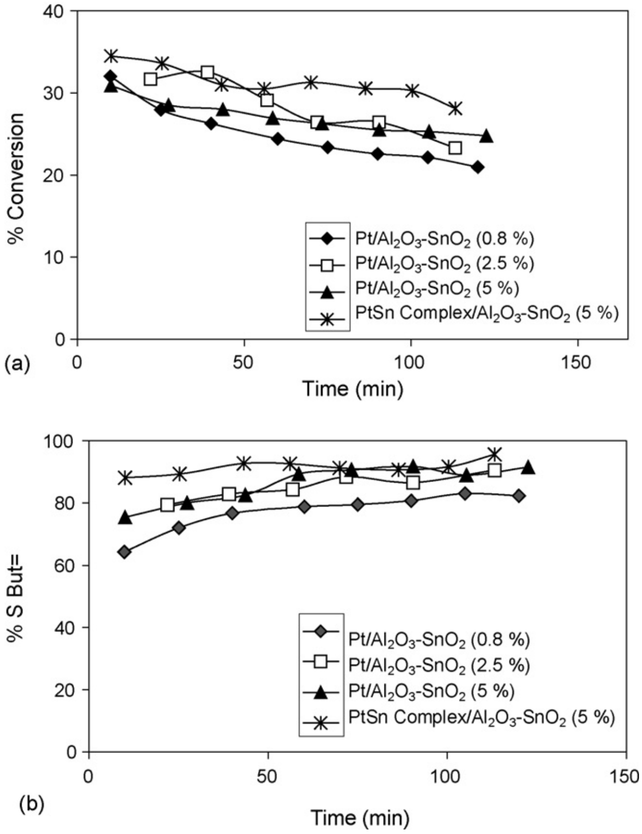

Fig. 6. Catalytic behavior in *n*-butane dehydrogenation of Pt and PtSn complex catalysts supported on Al_2O_3–SnO_2 (IES): (a) *n*-butane Conversion (%) and (b) selectivity to butenes (%).

Fig. 5 shows the XPS spectra corresponding to the Sn $3d_{5/2}$ level of Pt(0.3 wt%)/Al_2O_3–SnO_2(5%) and PtSn complex/Al_2O_3–SnO_2(5%) catalysts, respectively, after reduction ''in situ'' at 500 °C. From the deconvolution of the first spectrum, three peaks were obtained at 484.5, 486.2 and 487.6 eV, corresponding to different types of species. The component at lower binding energy corresponds to zerovalent Sn, while those corresponding to the second and third peak corresponds to different types of oxidized tin [23,24]. From the deconvolution of the second spectrum (corresponding to the PtSn complex), three peaks were also obtained at 484.6, 486.0 and 487.6 eV, corresponding to metallic tin and two different oxidized tin species, respectively. It must be noted that the percentages of zerovalent tin, though in low values (4% and 6% for Pt(0.3 wt%)/Al_2O_3–SnO_2(5%) and PtSn complex/Al_2O_3–SnO_2(5%) catalysts, respectively), would indicate the presence of metallic tin in both catalysts, which could be interacting with metallic Pt, with probable alloys formation. Similar low values of metallic tin were also observed recently by Serrano-Ruiz et al. [25] for PtSn/Al_2O_3 and PtSn/CeO_2–Al_2O_3 catalysts. It must be noted that the percentage of Sn(0) in the PtSn complex catalyst is higher than in the Pt(0.3 wt%)/Al_2O_3–SnO_2(5%) catalyst, thus indicating a higher PtSn interaction in the catalyst prepared with the complex. These results are in agreement with those found by chemisorption and test reactions.

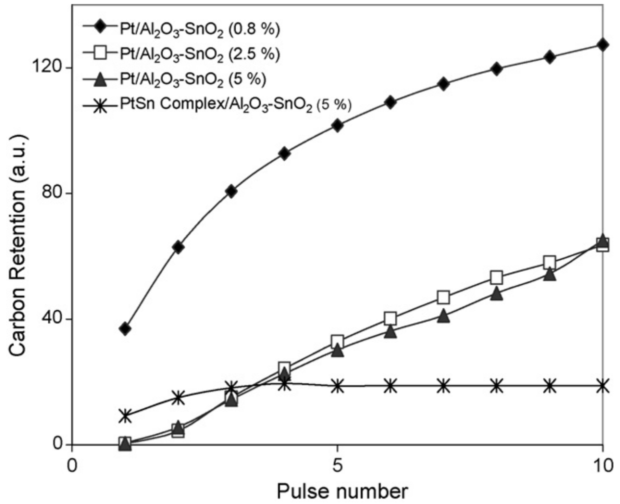

Fig. 7. Carbon retention during pulse experiments of *n*-butane in Pt and PtSn complex supported on Al_2O_3–SnO_2 (IES).

The catalytic behaviour (*n*-butane conversion and selectivity values to 1-butene, *cis*-2-butene, *trans*-2-butene and 1,3-butadiene) in flow experiments of Pt/Al_2O_3–SnO_2 (prepared by IES) in the butane dehydrogenation reaction is shown in Fig. 6. It can be observed an increase of the activity (Fig. 6(a)) and selectivities to butenes (Fig. 6(b)) for the catalysts with higher Sn contents. Besides, it must be noted that the catalyst prepared from the PtSn complex and supported on Al_2O_3–SnO_2 (5 wt% Sn) displays the highest activity and selectivity values (higher than 90%).

Moreover, the catalytic behaviour of the samples during the first stages of the reaction was determined by injection of *n*-butane pulses to the catalytic bed. Fig. 7 shows the amount of accumulative carbon deposited on the different catalysts as a function of the injected pulses. When increasing the tin content in the catalysts, the amount of deposited carbon is much lower. This carbon retention displays the lowest values in the case of catalysts prepared from the PtSn complex. This behaviour could be explained by the interaction between Pt and Sn that inhibits the carbon deposition during the first steps of the reaction, thus producing catalysts with a high catalytic stability. It must be noted that these results are in agreement with those obtained from the cyclopentane hydrogenolysis, since both reactions require similar ensembles.

4. Conclusions

Catalysts prepared by impregnation with Pt and a PtSn intermetallic complex on alumina modified with SnO_2 display an excellent behavior in activity, dehydrogenation selectivity (close to 90%) and stability during the reaction of butane dehydrogenation. The characterization of the metallic phase and the support (through TPR measurements, SEM, test reactions of the metallic and acidic phases, and chemisorption) would indicate the poisoning of the acid sites of alumina by tin addition, and the existence of geometric and probably electronic effects between Pt and Sn, with probable alloy formation. The Pt and Sn interaction would produce the inhibition of the carbon deposition and the hydrogenolysis reactions, with the consequence increase of the selectivity to dehydrogenation.

The catalyst prepared from the PtSn complex and supported on Al_2O_3–SnO_2 (5%) displays the higher interaction between both metals, and hence the highest activity and selectivity values (higher than 90%), and the lowest carbon retention during *n*-butane dehydrogenation reaction.

With respect to the better deposition method of high Sn concentrations, the impregnation of Sn in excess of solution would lead to a higher homogeneity in the tin distribution on the alumina surface, thus leading to catalysts with a better catalytic performance.

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