Characterization and catalytic behavior in the *n*-butane dehydrogenation of trimetallic InPtSn/MgAl$_2$O$_4$ catalysts

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Abstract

This paper deals with the characterization and catalytic dehydrogenation behavior of trimetallic InPtSn catalysts with different Sn content (from 0.12 wt% up to 1.08 wt%) supported on MgAl$_2$O$_4$. The support was initially impregnated with In, followed by a co-impregnation with Pt and Sn. The Pt and In contents in all catalysts were 0.30 wt% and 0.28 wt%, respectively. Besides, two catalysts with a Sn content of 0.37 wt% were prepared by two different methods: (a) successive impregnation (first Pt, second Sn) and (b) impregnation with PtSn complex, [(CH$_3$)$_4$N]$_2$[PtCl$_2$(SnCl$_3$)$_2$]. Experiments of *n*-butane dehydrogenation reaction were carried out both in continuous flow equipment and in pulse equipment. The catalysts were characterized by TPR, XPS and test reactions of the metallic phase. Trimetallic catalysts display high activity and selectivity to butenes and low deactivation during the *n*-butane dehydrogenation reaction. In order to analyze the influence of the preparation method on the catalytic performance, the better trimetallic catalyst was selected. It was observed that the different impregnation methods of Pt and Sn lead to trimetallic catalysts with similar catalytic behaviors between them. The characterization studies indicate the existence of geometric effects of In and Sn on Pt sites that produce a dilution of the Pt surface, and also a strong interaction between the three metals, which could lead to alloy formation. These facts positively influence the catalytic performance, thus increasing the activity, the selectivity to butenes and the stability of the metallic phase.

Keywords: Trimetallic PtSnIn catalysts; MgAl$_2$O$_4$ support; *n*-Butane dehydrogenation; Catalyst characterization

1. Introduction

The studies related with the use of ZnAl$_2$O$_4$ and MgAl$_2$O$_4$ as catalyst supports were increasing in the last years. In this sense, mono and bimetallic catalysts supported on these materials have been found to be active, selective and stable for the direct dehydrogenation of light paraffins. In fact, Padró et al. [1] found a very high selectivity to propylene in the propane dehydrogenation for PtSn/ZnAl$_2$O$_4$ and PtGe/ZnAl$_2$O$_4$ catalysts, and Bocanegra et al. [2,3] found excellent activity, selectivity and stability after several reaction–regeneration cycles in *n*-butane dehydrogenation for Pt catalysts supported on these spinels. At this respect, Rennard and Freel [4] found that the Pt/MgAl$_2$O$_4$ catalyst maintained a good Pt dispersion after several reaction–oxidation cycles (in propane and isopentane

dehydrogenation reactions). Armendariz et al. [5] reported a good selectivity of PtSn/MgAl$_2$O$_4$ catalysts in the isopentane dehydrogenation to isoamilenes. Bosch et al. [6] and Aguilar-Ríos et al. [7] also showed a good performance of Pt and PtSn catalysts supported on ZnAl$_2$O$_4$ in isobutane dehydrogenation. Taking into account these behaviors, it would be also possible to use these supports in catalysts for dehydrogenation of linear paraffins with high molecular weight in order to produce the corresponding mono-olefins. It must be also indicated that olefins have a very wide application in the production of polymers, intermediaries for detergents and additives for gasoline (MTBE) [8,9].

The use of ZnAl$_2$O$_4$ and MgAl$_2$O$_4$ as a support of dehydrogenation catalysts is based on their low acidic characteristics and very high thermal stability. The first characteristic is very important in paraffin dehydrogenation processes since a very high selectivity to olefins not only depends on an adequate structure of the metallic phase but also on the properties of the support in order to minimize the

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undesirable lateral reactions (such as cracking and coke formation) [1–7].

The study of tri and multimetallic catalysts is a new research field which has been applied for catalytic reforming [10,11] and other type of reactions [12–14], but not for light paraffins dehydrogenation. Moreover there are few papers about the characterization of mono and bimetallic catalysts supported on $MgAl_2O_4$ [2–5], and no work about tri or multimetallic catalysts supported on this spinel.

The objective of this paper is to determine the effect of the Sn and In addition to Pt supported on $MgAl_2O_4$ over the catalytic performance (activity, selectivity, catalyst deactivation and stability) in the *n*-butane dehydrogenation reaction carried out in flow and pulse equipments. Besides, a comparison between the properties of trimetallic catalysts prepared by using several Sn contents and different impregnation techniques of Pt and Sn (co-impregnation, successive impregnation and impregnation with a PtSn complex) is carried out. The metallic phase of the different catalysts were determined by different techniques: test reactions of the metallic phase (cyclohexane dehydrogenation and cyclopentane hydrogenolysis), temperature-programmed reduction (TPR) and X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Preparation and characterization of the support

$MgAl_2O_4$ was prepared by a solid phase reaction between MgO (purity 99.9955%) and γ-Al_2O_3 (purity 99.9%). The steps involved in the preparation of the support were (i) an intimate mixture of the reactants in the stoichiometric ratio (1 mol of MgO/mol γ-Al_2O_3); (ii) grinding of the mixture to obtain a talcum powder; (iii) formation of a paste by addition of distilled water to the powder; (iv) drying at 100 °C for 6 h; (v) calcination at 900 °C for 24 h. Then the solid was ground to a final particle size between 35 mesh and 80 mesh. The samples were characterized by X-ray diffraction (XRD) using a diffractometer Shimadzu with a radiation of Cu Kα (λ = 1.542 Å, V = 30 kV, I = 30 mA). The diffraction pattern obtained on this support was compared with those of $MgAl_2O_4$, γ-Al_2O_3 and MgO in order to determine the formation of the spinel and observe the possibility of the remaining impurities. By comparing the diffractograms, Fig. 1a shows the presence of the $MgAl_2O_4$ spinel, together with MgO impurities and traces of γ-Al_2O_3. In order to purify the spinel, seven washing steps were carried out by using 1.5 ml g^{-1} of aqueous solution of $(NH_4)_2CO_3$ 1 mol l^{-1}, followed by washing with deionized water and drying at 120 °C for 12 h. After this, a new diffractogram (Fig. 1b) shows the complete elimination of MgO.

The surface area (BET) and the pore volume of the purified $MgAl_2O_4$ were obtained by N_2 adsorption at −196 °C in a Quantachrome Corporation NOVA-1000 equipment. Results showed a specific surface area of 37 m^2 g^{-1} and a pore volume of 0.11 ml g^{-1}.

In order to characterize the acid properties of the $MgAl_2O_4$ support, isopropanol dehydration experiments in a continuous
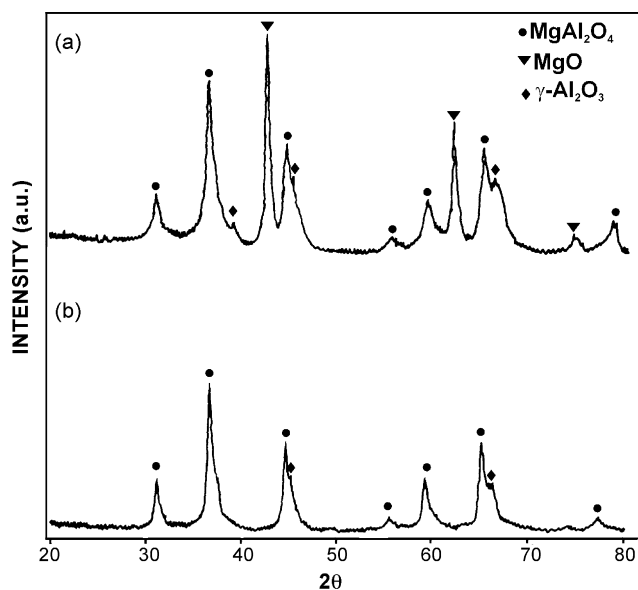

Fig. 1. X-ray diffractograms of non-purified $MgAl_2O_4$ (a) and purified $MgAl_2O_4$ (b).

flow reactor at atmospheric pressure were carried out. Prior to the reaction, samples were reduced "in situ" with H_2 at 500 °C. The alcohol was vaporized in a H_2 stream (H_2/isopropanol molar ratio = 19) and fed to the reactor with a space velocity of 0.52 mol alcohol h^{-1} g cat^{-1}. The sample weight was 100 mg and the reaction temperature was 200 °C. The acid properties of $MgAl_2O_4$ were determined by comparing dehydration activity of this support with that of γ-Al_2O_3 (taken as reference), which displays Lewis acidity [15] and an important dehydration conversion, such as Fig. 2 shows. This figure clearly displays the neutral characteristics of $MgAl_2O_4$ since it has a dehydration activity practically negligible. These results agree with the NH_3 TPD experiments carried out by Armendariz et al. [5].

The measurement of the equilibrium pH of $MgAl_2O_4$ suspended in water was performed by putting in contact the solid (1 g, 35/80 mesh) with 100 ml of deionised water at room temperature according to the technique reported by Roman-Martınez et al. [16]. The pH of the liquid phase was measured until the equilibrium value was reached (after 48 h). Values of
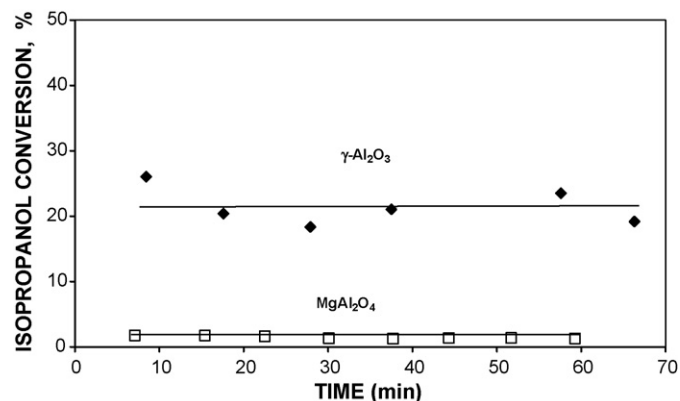

Fig. 2. Isopropanol conversion (%) vs. reaction time for $MgAl_2O_4$ and γ-Al_2O_3.

equilibrium pH between 8.2 and 8.6 were obtained, thus indicating the neutral properties of this support, in agreement with above-mentioned results.

2.2. Preparation of InPtSn catalysts

All the different trimetallic catalysts were prepared from one unique sample of In/MgAl$_2$O$_4$, by using different preparation methods. The In(0.28 wt%)/MgAl$_2$O$_4$ was prepared by incipient impregnation of MgAl$_2$O$_4$ with an aqueous solution of In(NO$_3$)$_3$ at room temperature for 6 h. The In concentration in the solution was 1.68 g l^{-1}, and the impregnating volume/support weight ratio was 2.0 ml g^{-1}. Then it was dried at 100 °C for 12 h. The InPtSn/MgAl$_2$O$_4$ catalysts were prepared by different methods and with different Sn loadings. Thus, PtSn catalysts supported on the In/MgAl$_2$O$_4$ were prepared by co-impregnation of the support with a solution containing H$_2$PtCl$_6$ and SnCl$_2$ in hydrochloric acid medium. The impregnation volume/mass of support was 1.4 ml g^{-1}. The Pt concentration was 2.1 g l^{-1} such as to obtain a Pt loading of 0.3 wt%. Different concentrations of the Sn were used in the co-impregnation: 0.84 g l^{-1}, 2.65 g l^{-1}, 5.29 g l^{-1} and 7.57 g l^{-1}, in order to obtain different Sn loadings in the catalysts: 0.12 wt%; 0.37 wt%; 0.74 wt% and 1.08 wt%, respectively. These catalysts were called as "C".

The second method used for the preparation of PtSn/In/MgAl$_2$O$_4$ was by successive impregnation. In this case the In/MgAl$_2$O$_4$ catalyst was first impregnated with an aqueous solution of H$_2$PtCl$_6$ at room temperature during 6 h. The impregnation volume/mass of support was 1.4 ml g^{-1}, and the Pt concentration (2.1 g l^{-1}) such as to obtain a Pt loading of 0.3 wt%. Then this solid was dried at 100 °C for 12 h. Then, the Pt/In/MgAl$_2$O$_4$ precursor was impregnated with an aqueous solution of SnCl$_2$ with hydrochloric acid. The concentration of Sn in the solution was 2.65 g l^{-1} to obtain a final loading of 0.37 wt% of Sn. After the Sn deposition, the precursor of the catalyst was dried at 100 °C for 12 h. This sample was called as "SI".

The third method used for the preparation of PtSn/In/MgAl$_2$O$_4$ catalyst was by a deposition of a PtSn complex on the In/MgAl$_2$O$_4$. In this case the complex [(CH$_3$)$_4$N]$_2$[PtCl$_2$(SnCl$_3$)$_2$] was synthesized according to the preparation method proposed by Antonov et al. [17]. Then this complex was dissolved in a hydrochloric solution before the impregnation of In/MgAl$_2$O$_3$. The impregnation conditions were: volume of the

impregnation solution/weight of support = 1.4 ml g^{-1} and concentration of complex in the solution = 9.43 g l^{-1}. The impregnation was carried out at room temperature for 6 h. In this way, a catalyst with 0.3 wt% of Pt and 0.37 wt% of Sn was obtained. After impregnation, the sample was dried at 100 °C for 12 h. This catalyst was named as "CX". In all cases, catalysts were calcined at 500 °C for 3 h. Table 1 compiles the different trimetallic catalysts, their preparation methods and nominal compositions.

Besides, monometallic Pt(0.3 wt%)/MgAl$_2$O$_4$, In(0.5 wt%)/MgAl$_2$O$_4$ and Sn(0.5 wt%)/MgAl$_2$O$_4$, and bimetallic Pt(0.3 wt%)Sn(0.3 wt%)/MgAl$_2$O$_4$ (prepared by co-impregnation) and In(0.28 wt%)Pt(0.3 wt%)/MgAl$_2$O$_4$ (successive impregnation, first In, second Pt) were prepared as references.

2.3. Reaction of n-butane dehydrogenation

Two different *n*-butane dehydrogenation tests were carried out, one of them in a continuous flow reactor and the other one in a pulse equipment. The continuous flow experiments were performed at 530 °C during 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*-C$_4$H$_{10}$ 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 530 °C under flowing H$_2$ for 3 h. The reactor effluent was analyzed in a GC-FID equipment with a packed chromatographic column (1/8″ × 6 m, 20% BMEA on Chromosorb P-AW 60/80) which was kept at 50 °C 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*/Σ mol 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

Table 1
Methods of preparation and nominal composition of the different catalysts

Catalyst	%In	%Pt	%Sn	Method
InPt/MgAl$_2$O$_4$	0.28	0.30	–	–
InPtSn(0.12)/MgAl$_2$O$_4$ C	0.28	0.30	0.12	Co-impregnation
InPtSn(0.37)/MgAl$_2$O$_4$ C	0.28	0.30	0.37	Co-impregnation
InPtSn(0.74)/MgAl$_2$O$_4$ C	0.28	0.30	0.74	Co-impregnation
InPtSn(1.08)/MgAl$_2$O$_4$ C	0.28	0.30	1.08	Co-impregnation
InPtSn(0.37)/MgAl$_2$O$_4$ SI	0.28	0.30	0.37	Successive impregnation (1° Pt, 2° Sn)
InPtSn(0.37)/MgAl$_2$O$_4$ CX	0.28	0.30	0.37	Complex PtSn

Base catalyst: In/MgAl$_2$O$_4$.

bed and the results showed a negligible *n*-butane conversion (≪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 as the sum of the carbon amount retained after each pulse.

2.4. Characterization of catalysts

The characteristics of the metallic catalysts were determined by different techniques: test reactions of the metallic phase (cyclohexane dehydrogenation and cyclopentane hydrogenolysis), temperature-programmed reduction (TPR) and X-ray photoelectron spectroscopy (XPS).

Cyclohexane dehydrogenation (CHD) and cyclopentane hydrogenolysis (CPH) were carried out in a differential flow reactor. Prior to these reactions, samples were reduced "in situ" with H$_2$ at 500 °C. In both reactions the H$_2$/hydrocarbon molar ratio was 26. The reaction temperatures in CHD were 450 °C, whereas in CPH the temperature was 500 °C.

TPR experiments were performed in a quartz flow reactor. The samples were heated at 6 °C min^{-1} from room temperature up to about 700 °C. The reductive mixture (5, v/v% H$_2$–N$_2$) was fed to the reactor with a flow rate of 10 ml min^{-1}. Catalysts were previously calcined "in situ" at 500 °C for 3 h.

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 "in situ" at 530 °C with H$_2$ for 2 h. Binding energies (BE) were referred to the C 1s peak at 284.9 eV. The peak areas were determined by fitting the experimental results with Lorentzian–Gaussian curves.

3. Results and discussion

In order to determine the oxidation state of the different metals in the trimetallic catalysts after reduction at 500 °C, XPS
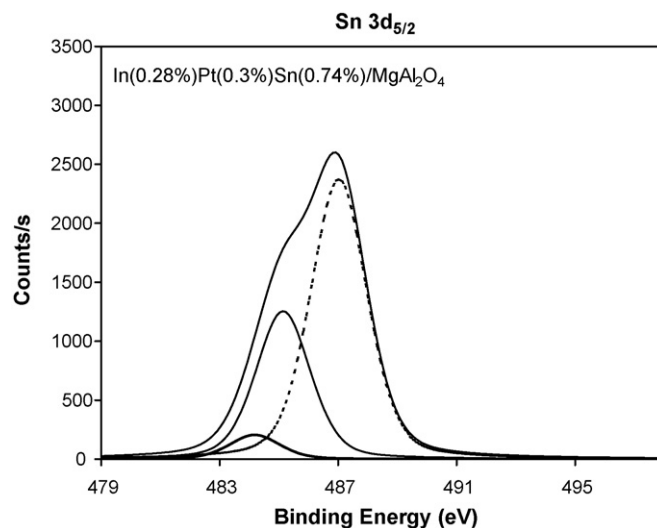
Fig. 3. XPS spectra corresponding to the Sn 3d$_{5/2}$ level for In (0.28%)Pt(0.3%) Sn(0.74%)/MgAl$_2$O$_4$ (prepared by co-impregnation of Pt and Sn) catalyst, previously reduced at 530 °C.

characterization was carried out. XPS spectra of the Pt 4f level for In(0.28 wt%)Pt(0.3 wt%)Sn(0.74 wt%)/MgAl$_2$O$_4$ and In(0.28 wt%)Pt(0.3 wt%)Sn(1.08 wt%)/MgAl$_2$O$_4$ catalysts, both prepared by co-impregnation, show the doublets corresponding to zerovalent Pt 4f signals separated at 3.36 eV between them [18].

Fig. 3 shows the XPS spectra corresponding to the Sn 3d$_{5/2}$ level of In(0.28 wt%)Pt(0.3 wt%)Sn(0.74 wt%)/MgAl$_2$O$_4$ catalyst after reduction "in situ" at 500 °C. From the deconvolution of the spectrum, three peaks were obtained at 484.2 eV, 485.2 eV and 487.1 eV, corresponding to different types of species. The component at lower binding energy (484.2 eV) corresponds to zerovalent Sn, and that located at 485.2 eV could be assigned to alloyed tin, while the third peak corresponds to oxidized species of tin(II, IV) (487.1 eV), in agreement with XPS results observed by Homs et al. [14,19].
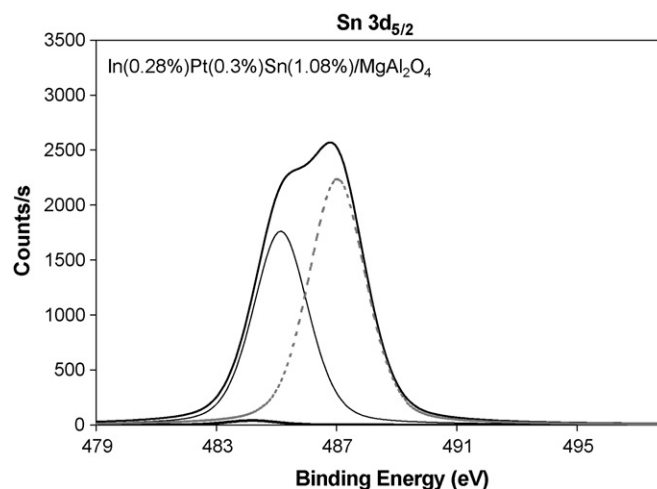
Fig. 4. XPS spectra corresponding to the Sn 3d$_{5/2}$ level for In (0.28%)Pt(0.3%) Sn(1.08%)/MgAl$_2$O$_4$ catalyst (prepared by co-impregnation of Pt and Sn), previously reduced at 530 °C.

Table 2
Results of reaction rates for cyclohexane dehydrogenation and cyclopentane hydrogenolysis for different catalysts

Catalysts	R_{CH} (mol h^{-1} g Pt^{-1}) $T = 450\ °C$	R_{CP} (mol h^{-1} gPt^{-1}) $T = 500\ °C$
Pt/MgAl$_2$O$_4$	496	8
InPt/MgAl$_2$O$_4$	138	Negligible
PtSn/MgAl$_2$O$_4$	141	4.9
InPtSn(0.12 wt%)/MgAl$_2$O$_4$	97	Negligible
InPtSn(0.37 wt%)/MgAl$_2$O$_4$	11	Negligible
InPtSn(0.74 wt%)/MgAl$_2$O$_4$	3	Negligible
InPtSn(1.08 wt%)/MgAl$_2$O$_4$	Negligible	Negligible

Fig. 4 shows the XPS spectra corresponding to the Sn 3d$_{5/2}$ level of In(0.28 wt%)Pt(0.3 wt%)Sn(1.08 wt%)/MgAl$_2$O$_4$ catalyst after reduction ''in situ'' at 500 °C. From the deconvolution of the spectrum, three peaks were also obtained at 484.1 eV, 485.1 eV and 487.0 eV, corresponding to zerovalent, alloyed and oxidized tin, respectively [14,19]. It must be noted that the percentages of metallic and alloyed tin, obtained as the sum of the areas corresponding to the first and second peaks, are very important (50% and 30% for InPtSn(0.74 wt%)/MgAl$_2$O$_4$ and InPtSn(1.08 wt%)/MgAl$_2$O$_4$, respectively).

The different catalysts were evaluated in the cyclohexane dehydrogenation reaction, which is a structure insensitive one [20] and the results are shown in Table 2. Benzene was the only product observed for all the catalysts, and no deactivation was detected. It must be noted that monometallic In/MgAl$_2$O$_4$ and Sn/MgAl$_2$O$_4$ catalyst were inactive for this reaction, while the monometallic Pt/MgAl$_2$O$_4$ one is very active. The addition of the second metal (In or Sn) to Pt decreased the dehydrogenation activity, whereas the joint addition of Sn and In to Pt also decreased the activity, but in a greater degree. It is observed that the trimetallic catalyst with the higher tin content has negligible activity. The activation energies for this reaction were calculated for Pt/MgAl$_2$O$_4$, PtSn/MgAl$_2$O$_4$ PtIn/MgAl$_2$O$_4$ catalysts by carrying out experiments at 300 °C, 285 °C and 270 °C. Unfortunately, at these low temperatures, trimetallic catalysts were inactive. Results showed similar activation energies values (20 kcal mol^{-1}) for Pt/MgAl$_2$O$_4$ and InPt/MgAl$_2$O$_4$ catalysts, and a higher value (23 kcal mol^{-1}) for PtSn/MgAl$_2$O$_4$, which indicate that the tin addition would modify electronically to platinum. On the other hand, the effect of indium to platinum would be different, probably by diluting and blocking the platinum sites, such as was proposed by Passos et al. [21].

The behavior of the catalysts in the cyclopentane hydrogenolysis reaction, which is a structure-sensitive one [22] displays that the monometallic Pt/MgAl$_2$O$_4$ is active for this reaction (Table 2). It must be noted that monometallic In/MgAl$_2$O$_4$ and Sn/MgAl$_2$O$_4$ catalysts were inactive in this reaction. The addition of Sn to Pt produces an important diminution of the hydrogenolytic ensembles, whereas the incorporation of In completely eliminates these ensembles, since the activity of InPt/MgAl$_2$O$_4$ catalyst is undetectable. Besides the hydrogenolytic activity of all the trimetallic catalysts is negligible. These results could be interpreted taking into account that as this reaction requires larger Pt ensembles to be carried out, the presence of the promoter modifies geometrically the metallic phase and produces a dilution of the surface Pt. The effect of In on the hydrogenolytic activity is more pronounced than the influence of Sn, thus indicating that In dilutes the Pt atoms more homogeneously than Sn, as it was already mentioned. In the trimetallic catalysts, the combined effect of In and Sn produces the complete elimination of the hydrogenolytic ensembles.

The TPR profile of the fresh monometallic Pt/MgAl$_2$O$_4$ catalyst (Fig. 5) shows a main reduction peak at 265 °C and a small peak at about 460 °C. The presence of two reduction peaks was also observed in Pt/Al$_2$O$_3$ catalysts and it was explained by the existence of two different oxychlorinated Pt species originated after the impregnation of the support with chloroplatinic acid and the subsequent thermal treatments (drying and calcination steps) [23]. The TPR profile of the fresh Sn(0.5 wt%)/MgAl$_2$O$_4$ catalyst shows a small, non-well-defined reduction zone at high temperatures (>550 °C). Besides the TPR profile of the fresh In(0.5 wt%)/MgAl$_2$O$_4$ catalyst shows a reduction zone at temperatures higher than 550 °C. The reduction profile of the trimetallic In(0.5 wt%)Pt(0.3 wt%)Sn(1.08 wt%)/MgAl$_2$O$_4$ catalyst displays a very big and well-defined peak at about 335 °C, and a small shoulder at temperatures between 450 °C and 550 °C. The width of the main peak and its shift to higher temperatures indicate the co-reduction of Pt with the other metals (Sn and In), which suggests a strong interaction between the metals with probable alloy formation. In this sense Homs et al. found (by TEM and EDX characterization) large trimetallic particles corresponding to PtSn$_{1-x}$In$_x$ alloys in PtSnIn/SiO$_2$ catalysts [14].
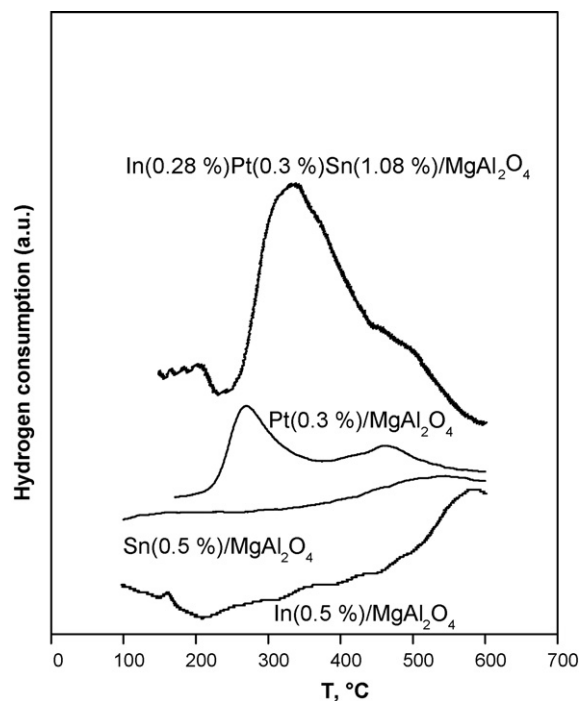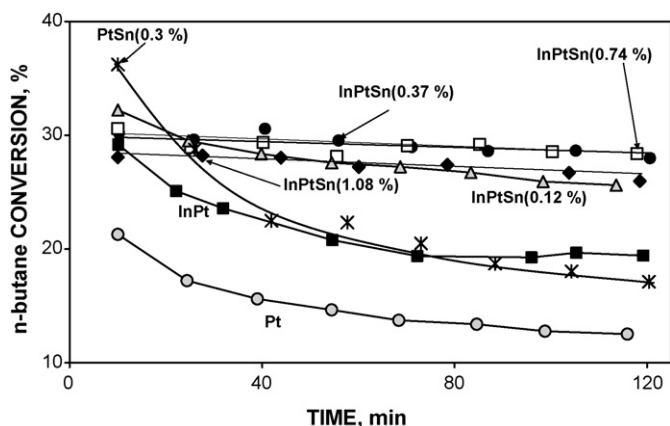

Fig. 5. TPR profiles of the different catalysts.

Fig. 6. *n*-Butane conversion (%) vs. reaction time for different catalysts prepared by co-impregnation of Pt and Sn. The deactivation parameter (ΔX) is defined as $\Delta X = 100 \times (X_f - X_0)/X_0$, where X_0 is the initial conversion (at 10 min of reaction time) and X_f is the final conversion (at 120 min of the reaction time). ΔX values for different catalysts: Pt/MgAl$_2$O$_4$ (ΔX = 40.9%), PtSn(0.3%)/MgAl$_2$O$_4$ (ΔX = 51.5%), InPt/MgAl$_2$O$_4$ (ΔX = 33.2%), InPtSn(0.12%)/MgAl$_2$O$_4$ (ΔX = 20.5%), InPtSn(0.37%)/MgAl$_2$O$_4$ (ΔX = 6.7%), InPtSn(0.74%)/MgAl$_2$O$_4$ (ΔX = 7.0%), InPtSn(1.08%)/MgAl$_2$O$_4$ (ΔX = 6.7%).

The results of cyclohexane dehydrogenation, XPS and TPR for trimetallic catalysts clearly show of the existence of strong metal interactions, with probable alloy formation. Besides, geometric effects (blocking and dilution of active Pt sites by Sn and mainly by In) are also important, such as it was observed in cyclopentane hydrogenolysis results.

Fig. 6 shows the butane conversion as a function of the reaction time in a flow reactor for different monometallic (Pt/MgAl$_2$O$_4$), bimetallic (InPt/MgAl$_2$O$_4$ and PtSn/MgAl$_2$O$_4$), and trimetallic InPtSn/MgAl$_2$O$_4$ catalysts (prepared by co-impregnation and with different Sn contents). The deactivation parameter (ΔX) along the reaction time was defined as: $\Delta X = 100 \times (X_f - X_0)/X_0$, where X_0 is the initial conversion (at 10 min of reaction time) and X_f is the final conversion (at 120 min of the reaction time). The Pt/MgAl$_2$O$_4$ catalyst displays a low initial conversion (21%) and a high deactivation parameter (41%), and the bimetallic InPt/MgAl$_2$O$_4$ catalyst shows a higher initial conversion (28%) and lower deactivation parameter. The indium addition to platinum improves the stability of the monometallic catalyst, and this effect would be related with the decrease of the ensembles required for the carbon formation in this catalysts. It must be noted that similar ensembles are necessaries both for carbon formation and for hydrogenolysis, and these hydrogenolytic ensembles practically disappear after indium addition to platinum, such as it is observed in Table 2. The PtSn/MgAl$_2$O$_4$ catalyst shows a much higher initial conversion (37%), but the deactivation parameter along the reaction time remains very high (51%). On the other hand, the tin addition to InPt/MgAl$_2$O$_4$ catalyst shows both a pronounced increase of the initial conversion (28–32%) and an important decrease of the deactivation parameter (<10%), except for the trimetallic catalyst with the lower Sn content which shows a ΔX of about 21%. Besides, at the higher Sn content (1.08 wt%), there is an excellent stability, but the values of the conversion along the reaction time are lower than for the
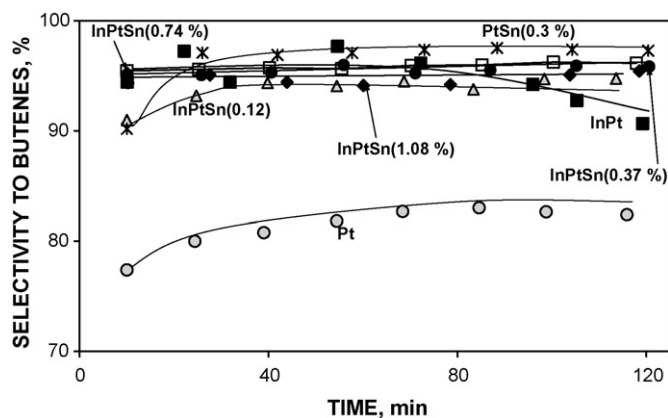

Fig. 7. Selectivity (%) to the different butenes (1-butene, *cis*-2-butene, *trans*-2-butene and 1,3-butadiene) vs. reaction time for different catalysts prepared by co-impregnation of Pt and Sn.

catalysts with tin contents of 0.37 wt% and 0.74 wt%. Hence these catalysts with intermediate tin contents have the better performance in catalytic activity, with high values of initial conversion and very low deactivation.

Fig. 7 shows the selectivity values to butenes obtained by the different catalysts. Both the trimetallic InPtSn (with different tin contents) and the bimetallic InPt and PtSn catalysts supported on MgAl$_2$O$_4$ display high selectivities, between 91% and 97%, while the monometallic Pt/MgAl$_2$O$_4$ shows selectivities lower than 84%. From these results, In and Sn additions produce an important increase of the selectivity values to butenes.

The initial and final yields to butenes for the four trimetallic catalysts are shown in Table 3. The yield is defined as the product between the butane conversion and the selectivity to butenes. From Figs. 6 and 7 and Table 3, and taking into account the excellent catalytic performance in the *n*-butane dehydrogenation of the catalysts with Sn contents of 0.37 wt% and 0.74 wt%, the catalyst with lower tin concentration (0.37 wt%) was chosen to study the influence of the method of impregnation used to prepare these catalysts.

Fig. 8 shows the catalytic behavior (butane conversion and selectivity to the different butenes) in a continuous flow reactor of the trimetallic catalysts with Sn content of 0.37 wt%, prepared by using different impregnation techniques: co-impregnation (C) (1st In, 2nd Pt + Sn), successive impregnation (SI) (1st In, 2nd Pt, 3rd Sn) and impregnation with a PtSn complex (CX) (1st In, 2nd PtSn complex). The values of conversion and selectivity are

Table 3
Initial and final yields (Y) to butenes for the trimetallic catalysts prepared by co-impregnation (C)

Catalysts	Y % initial (at 10 min)	Y % final (at 120 min)
InPtSn(0.12 wt%)/MgAl$_2$O$_4$	29	24
InPtSn(0.37 wt%)/MgAl$_2$O$_4$	29	27
InPtSn(0.74 wt%)/MgAl$_2$O$_4$	29	27
InPtSn(1.08 wt%)/MgAl$_2$O$_4$	27	25

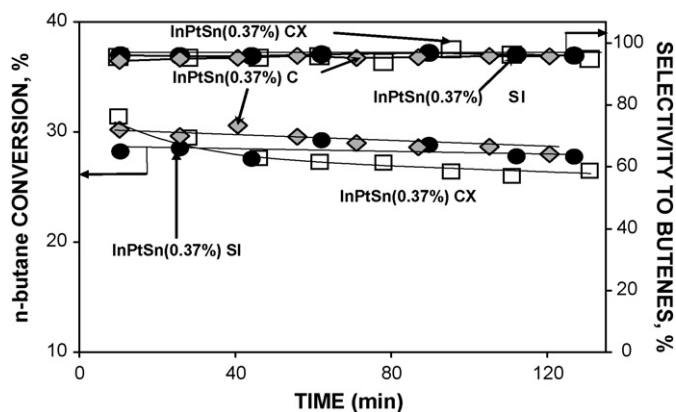Yield is defined as the product between the butane conversion and the selectivity to butenes.

Fig. 8. *n*-Butane conversion (%) and selectivity (%) to the different butenes (1-butene, *cis*-2-butene, *trans*-2-butene and 1,3-butadiene) vs. reaction time for InPtSn(0.37%)/MgAl₂O₄ catalysts prepared by co-impregnation (C, ◆), successive impregnation (SI, ●) and impregnation with PtSn complex (CX, □).
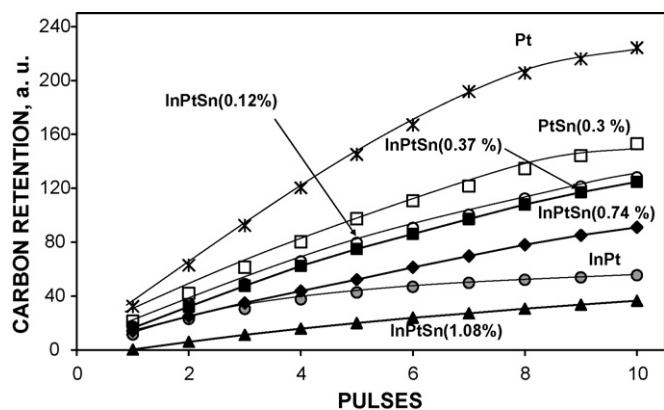

Fig. 10. Carbon retention as a function of the number of *n*-butane pulses injected to the Pt/MgAl₂O₄ sample (○) and to the trimetallic InPtSn (0.37%)/MgAl₂O₄ catalysts prepared by co-impregnation (C, ◆), successive impregnation (SI, ●) and impregnation with PtSn complex (CX, □).

Fig. 9. Carbon retention as a function of the number of *n*-butane pulses injected to the mono and bimetallic Pt/MgAl₂O₄ (✳), InPt/MgAl₂O₄ (◉) and PtSn/MgAl₂O₄ (□) samples and to the different trimetallic catalysts prepared by co-impregnation: InPtSn(0.12%)/MgAl₂O₄ (○), InPtSn(0.37%)/MgAl₂O₄ (■), InPtSn(0.74%)/MgAl₂O₄ (◆), InPtSn(1.08%)/MgAl₂O₄ (▲).

similar for the three catalysts, displaying all of them conversions between 27% and 31%, a very low deactivation parameter, and selectivities higher than 94%.

In order to study the behavior of the catalysts in the first stages of the reaction, pulse experiments of *n*-butane injected to the catalytic bed were carried out at the same reaction temperature than for flow experiments (530 °C). In this sense, it can be observed in Figs. 9 and 10 the behavior of the catalysts with respect to the carbon retention along the injected pulses. This carbon retention was obtained through a mass balance of C moles. The monometallic Pt/MgAl₂O₄ catalyst displays the highest carbon retention. Tin addition to Pt/MgAl₂O₄ slightly decreases the coke deposition, while indium addition to platinum drastically diminishes the carbon formation along the 10 injected pulses. This geometric effect of indium on platinum is in agreement with flow *n*-butane dehydrogenation and cyclopentane hydrogenolysis results. The trimetallic InPtSn/MgAl₂O₄ catalysts display in general low carbon retention, which decreases as the tin content increases (Fig. 9). By comparing the different preparation techniques used to prepare
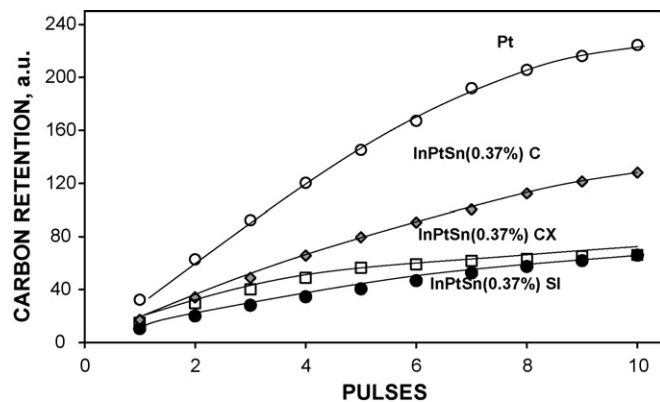
the trimetallic catalysts, it would observe slightly higher carbon formation for catalysts prepared by the co-impregnation method than for successive impregnation and impregnation with the complex ones (Fig. 10).

4. Conclusions

Tin and indium addition to Pt in catalysts supported on MgAl₂O₄ produces important increases of the butane conversion and the selectivity to olefins, and an important decrease of the carbon deposition (main cause of the catalyst deactivation), thus leading to an excellent performance in the *n*-butane dehydrogenation reaction.

There is practically no influence of the different impregnation ways used for the preparation of the trimetallic catalysts (successive impregnation, co-impregnation and impregnation with a PtSn complex) on the catalytic behavior of the catalysts.

The characterization studies of the trimetallic catalysts display a strong interaction between the different metals, which could be responsible of the very good performance of these PtSnIn/MgAl₂O₄ catalysts. Besides, the presence of the In and Sn modifies geometrically the metallic phase, thus producing a dilution of the Pt surface, and hence the elimination of the ensembles for hydrogenolytic reactions and carbon formation.

References

[1] C.L. Padró, S.R. de Miguel, A.A. Castro, O.A. Scelza, Stud. Surf. Sci. Catal. 111 (1997) 191.

[2] S.A. Bocanegra, A. Guerrero-Ruíz, S.R. de Miguel, O.A. Scelza, Appl. Catal. A: Gen. 277 (2004) 11.

[3] S.A. Bocanegra, S.R. de Miguel, A.A. Castro, O.A. Scelza, Catal. Lett. 96 (3/4) (2004) 129.

[4] R.J. Rennard, J. Freel, J. Catal. 98 (1986) 235.

[5] H. Armendariz, A. Guzmán, A. Toledo, M.A. Llanos, A. Vázquez, G. Aguilar, Appl. Catal. A: Gen. 211 (2001) 69.

[6] P. Bosch, M.A. Valenzuela, B. Zapata, D. Acosta, G. Aguilar-Ríos, C. Maldonado, I. Shifter, J. Mol. Catal. 93 (1994) 67.

[7] G. Aguilar-Ríos, M.A. Valenzuela, H. Armendáriz, P. Salas, J.M. Domínguez, D.R. Acosta, I. Schifter, Appl. Catal. A: Gen. 90 (1992) 25.

[8] L.F. Hatch, S. Matar, From Hydrocarbons to Petrochemicals, Gulf Publishing Company, Houston, 1981.

[9] A.V. Hahn (Editor), The Petrochemical Industry, Mc Graw-Hill Inc., New York, 1970.

[10] Á. Fürcht, A. Tungler, S. Szabó, A. Sárkány, Appl. Catal. A: Gen. 226 (2002) 155.

[11] C. Carnevillier, F. Epron, P. Marecot, Appl. Catal. A: Gen. 275 (2004) 25.

[12] S. Hermans, M. Devillers, Appl. Catal. A: Gen. 235 (2002) 253.

[13] B. Franck, G. Emig, A. Renken, Appl. Catal. B: Environ. 19 (1) (1998) 45.

[14] N. Homs, J. Llorca, M. Riera, J. Jolis, J. Fierro, J. Sales, P. Ramírez de la Piscina, J. Mol. Catal. A: Chem. 200 (2003) 251.

[15] R. Fiedorow, I.G. DallaLana, J. Phys. Chem. 84 (1980) 2779.

[16] M.C. Román-Martınez, D. Cazorla-Amoros, A. Linares-Solano, C. Salinas Martınez de Lecea, H. Yamashita, N. Ampo, Carbon 33 (1995) 3.

[17] P.G. Antonov, Yu.N. Nukushkin, V.G. Shtrele, Yu.P. Kostikov, F.K. Egorov, Zh. Neorg. Khim. SSSR 27 (1982) 3130.

[18] C.D. Wagner, W.M. Riggs, L.E. Davis, J.F. Moulder, Handbook of X-ray Photoelectron Spectroscopy, 1993.

[19] J. Llorca, P. Ramirez de la Piscina, J.L.G. Fierro, J. Sales, N. Homs, J. Mol. Catal. A 118 (1997) 101.

[20] A.D. Cinneide, J.K.A. Clarke, Catal. Rev. 7 (1972) 233.

[21] F.B. Passos, D.A. Aranda, M. Schmal, J. Catal. 178 (1998) 478.

[22] M. Boudart, Adv. Catal. 20 (1969) 153.

[23] G. Lietz, H. Lieske, H. Spindler, W. Hanke, J. Volter, J. Catal. 81 (1983) 17.