

n-Butane dehydrogenation on PtSn supported on MAl_2O_4 (M: Mg or Zn) catalysts

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A study about the performance of PtSn supported on MAl_2O_4 (M: Mg or Zn) catalysts with low metals loadings (0.3 wt.% Pt, 0.3–0.5 wt.% Sn) in *n*-butane dehydrogenation is reported in this paper. Catalysts were tested in flow and pulse equipments. Besides, reaction-regeneration cycles were performed in order to determine the catalytic stability. Results showed that the Sn addition enhances the catalytic properties, the influence being almost negligible for both supports when the Sn content increases from 0.3 to 0.5 wt.%. The bimetallic formulations supported on MgAl_2O_4 showed a better stability in the reaction-regeneration cycles than those supported on ZnAl_2O_4 , this behavior being related to a higher stability of the metallic phase of the PtSn/ MgAl_2O_4 catalysts after the cycles as TPR results show.

KEY WORDS: PtSn-supported catalysts; *n*-butane dehydrogenation; ZnAl_2O_4 and MgAl_2O_4 supports.

1. Introduction

The dehydrogenation of light paraffins to olefins also produces undesirable lateral reactions which lead to both light products (C_1 , C_2 , etc) and coke deposition that decrease the olefin yields. The use of supported noble metals, like Pt, modified by the addition of inactive metals (like Sn, Pb, Ga) improves the catalytic performance [1,2]. Jablonski *et al.* [3] reported that the Ga addition to Pt/ Al_2O_3 catalyst enhances the yield to propylene (in propane dehydrogenation) due to an increase mainly of the selectivity to propylene which reaches values close to 90%, but the deactivation only decreases from about 70% for the monometallic catalyst to 60% for the bimetallic ones. These authors indicated that the Ga addition has a low effect on the acidity of the support. It was also observed by Loc *et al.* [4] that the addition of a second metal (In or Sn) to Pt/K-doped Al_2O_3 increases the reaction rate and the selectivity to propylene in the propane dehydrogenation. Other authors indicated that the PtSn/ Al_2O_3 catalyst shows an activity similar to the monometallic one, but the selectivity to olefins is increased with respect to the Pt/ Al_2O_3 catalysts [5]. Besides, it was reported in the literature [6] that the Sn addition to a Pt/ SiO_2 catalyst leads to a decrease of the interaction between Pt and C_3H_6 . These authors also found a simultaneous poisoning effect of Sn on the surface acidic sites with the consequent diminution of the carbon deposition. The use of neutral or non-acidic supports such as Zn or Mg spinels could be a good alternative to enhance the

selectivity to mono-olefins, since the undesirable reactions on the acidic function (hydrocracking and coke formation) could be suppressed [7–9]. These supports can be obtained by different preparation techniques, and its application as supports of metallic catalysts for dehydrogenation processes shows that the catalytic behavior appears to depend not only on the preparation method of the supports and the metallic supported catalysts, but also on the Pt content and the Sn/Pt molar ratio as well. At this respect, Rennard and Freel [10] found that the Pt/ MgAl_2O_4 catalyst maintained a good Pt dispersion after six reaction-oxidation cycles (in propane and iso-pentane dehydrogenation reactions). Bosch *et al.* [7] found that PtSn/ ZnAl_2O_4 catalysts display a high thermal stability, but the addition of higher amounts of Sn (> 1 wt.%) to Pt(0.5 wt.)/ ZnAl_2O_4 would produce the formation of different PtSn alloys along with a surface Sn enrichment of the metallic phase, which would inhibit the catalytic activity in isobutane dehydrogenation. Moreover, a promoting effect of low amounts of Sn added to the Pt/ ZnAl_2O_4 catalyst was also found by Pakhomov *et al.* [11], but higher Sn amounts added to Pt decreases the catalytic activity. This effect was attributed to the formation of PtSn alloys at higher Sn contents. A topic partially explored in the literature is related to the stability of PtSn alloys under different atmospheres. In this sense Pakhomov *et al.* [8] reported that the oxidation treatment of PtSn/ ZnAl_2O_4 catalysts would transform the PtSn alloys into metallic Pt and SnO_2 .

The objective of the present paper is focused on the study of the performance of PtSn/ MAl_2O_4 catalysts (M: Mg or Zn) with low metal contents (0.3 wt.% Pt and 0.3–0.5 wt.% Sn). Supports were prepared at the

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laboratory by using the technique reported by Strohmeier and Hercules [12]. In this case, a special emphasis was focused not only on the study of the support effect and the Sn content on the activity and selectivity, but also on the stability through successive operative cycles (reaction-regeneration-reaction) in the *n*-butane dehydrogenation reaction. Moreover, a detailed study of the initial reaction steps by using a pulse technique is presented in order to explain the different catalytic behaviors.

2. Experimental

In this study, metals (Pt and Sn) were supported on two different materials: ZnAl₂O₄ and MgAl₂O₄, both prepared at the laboratory. A solid phase reaction method proposed by Strohmeier and Hercules [12] was used for the preparation of these supports. For the preparation of ZnAl₂O₄, ZnO (99.9% from Analab R) and γ -Al₂O₃ (99.9%) were the reactants, while for MgAl₂O₄, MgO (99.995% from Alfa) was used instead ZnO. These reactants were mixed in a stoichiometric proportion and then ground to a very fine powder. Then, deionized water was added to this mixture to obtain a paste, which was dried at 373 K during 6 h and then calcined at 1173 K during 72 h. At this temperature the reaction between ZnO (or MgO) with γ -Al₂O₃ takes place. The solids thus prepared were ground to 35/80 mesh. In order to determine the formation of the respective ZnAl₂O₄ (or MgAl₂O₄) compounds, XRD spectra were obtained. The small amounts of MgO or ZnO remaining in these materials were eliminated by a purification treatment with an aqueous solution of (NH₄)₂CO₃ 1 M (five washing steps with 1.5 mL solution g⁻¹ support), and then the solid was dried at 373 K. XRD measurements were also carried out on the purified samples. All XRD measurements were performed in a Shimadzu diffractometer with a CuK α radiation ($\lambda = 1.542 \text{ \AA}$), voltage: 30 kV and current: 30 mA.

Specific surface areas of the supports were determined in a Quantachrome Corporation NOVA-1000 surface area analyzer, by using N₂ as an adsorbate.

The measurement of the equilibrium pH of MgAl₂O₄ suspended in water was performed by putting in contact the solid (1 g, 35/80 mesh) with 100 mL of deionized water at room temperature following the technique reported by Román-Martínez *et al.* [13]. The pH of the liquid phase was measured until the equilibrium value was reached (about 48 h).

The following catalysts were used for this study: Pt/ZnAl₂O₄, PtSn(0.3 wt%)/ZnAl₂O₄, PtSn(0.5 wt%)/ZnAl₂O₄, Pt/MgAl₂O₄, PtSn(0.3 wt%)/MgAl₂O₄ and PtSn(0.5 wt%)/MgAl₂O₄. In all cases the Pt content was 0.3 wt%.

Monometallic catalysts were prepared by impregnation of the corresponding support with an aqueous

solution of H₂PtCl₆. For the impregnation of ZnAl₂O₄, the Pt concentration in the impregnating solution was 4.3 g L⁻¹ and the impregnating volume/support weight ratio was 0.7 mL g⁻¹. In the case of the impregnation of MgAl₂O₄, the Pt concentration in the impregnating solution was 2.15 g L⁻¹ and the impregnating volume/support weight ratio was 1.4 mL g⁻¹. In both cases impregnations were carried out at room temperature during 6 h. After impregnation, samples were dried at 383 K during 12 h.

Bimetallic catalysts were obtained by the impregnation of the monometallic ones with a hydrochloric solution of SnCl₂ (1.2 M HCl). The Sn concentrations in the solution were: 4.28 g L⁻¹ and 7.14 g L⁻¹ for the impregnation of the Pt/ZnAl₂O₄ catalyst with 0.3 and 0.5 wt% Sn, respectively. In the case of the impregnation of the Pt/MgAl₂O₄ catalyst with Sn, the concentrations were 2.14 g Sn L⁻¹ for 0.3 wt% Sn and 3.57 g Sn L⁻¹ for 0.5 wt% Sn. The ratio between the volume of the SnCl₂ solution and the weight of the monometallic catalyst was 0.7 mL g⁻¹ for Pt/ZnAl₂O₄ and 1.4 mL g⁻¹ for Pt/MgAl₂O₄. After the impregnation with the tin solution (6 h, 298 K), samples were dried at 383 K overnight. Then, the mono and bimetallic catalysts were calcined at 773 K during 3 h (labeled as fresh samples).

The different catalysts were evaluated in the *n*-butane dehydrogenation reaction by two different tests, one of them in a continuous flow reactor and the other one in a pulse equipment.

Continuous flow experiments were performed 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, H₂/*n*-C₄H₁₀ molar ratio = 1.25). The reactive mixture was prepared *in situ* by using mass flow controllers. All gases, *n*-butane, N₂ (used for purge), and H₂ (used for both the previous reduction of catalysts and the reaction) were high purity ones (>99.99%). The reactor effluent was analyzed by a GC-FID equipment. The chromatographic column (1/8" × 6 m) used for these analysis was a packed one (20% BMEA on Chromosorb P-AW 60/80). The column was maintained at 323 K during the analysis. With this analytical device, methane, ethane, ethylene, propane, propylene, *n*-butane, 1-butene, cis-2-butene, trans-2-butene and 1-3 butadiene can be detected. The *n*-butane conversion was calculated as the sum of the percentages of the chromatographic areas of all the reaction products affected by the corresponding response factor (except H₂). The selectivity to the different reaction products (i) was defined as the ratio: mol of product i/Σ mol of all products (except H₂). Taking into account the high temperatures (773–853 K) used for the reaction (for thermodynamic reasons), it was necessary to determine the contribution of the homogeneous reaction. In this way a blank experiment was performed by using a

quartz bed (0.200 g). Results showed that a negligible *n*-butane conversion was obtained ($\ll 1\%$). Hence, the incidence of the homogeneous phase reaction can be discarded in the overall range of the reaction temperature used in this work.

Pulse experiments were carried out in order to study with more details the initial steps of the *n*-butane dehydrogenation reaction with respect to the carbon deposition and its relationship with the *n*-butane conversion, the catalyst deactivation and the selectivity to different products as well. These experiments were performed by injecting pulses of pure *n*-butane (0.5 mL STP) to the catalytic bed (0.100 g of sample) maintained at 803 K. The catalytic bed was kept under flowing He (30 mL min⁻¹) between the injection of two successive pulses of *n*-butane. The composition of the pulse after the reaction was determined by using a GC-FID with a packed column (Porapack Q). The temperature of the chromatographic column was 303 K. Previous to the experiments all samples were reduced *in situ* under flowing H₂ at 803 K during 3 h. 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, and this difference was referred to the chromatographic area of *n*-butane fed to reactor. The selectivity to a given product was calculated in the same way as for flow experiments. The carbon amount retained on the catalyst after injecting each pulse was calculated through a carbon mass balance between the total carbon amount fed to 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 retention in each pulse.

Besides the above mentioned test in *n*-butane dehydrogenation, studies on the catalytic stability of the bimetallic PtSn(0.3 wt%)/ZnAl₂O₄ and PtSn(0.3 wt%)/MgAl₂O₄ catalysts were carried out. These stability studies consisted on several reaction-regeneration cycles. The sequence was the following: reaction (at 803 K, 6 h), purge with N₂, regeneration by using an O₂-N₂ (5 % v/v O₂) mixture, purge with N₂, and reduction with H₂ at 803 K. This sequence was repeated five times. The purge steps with N₂ were performed at 673 K during 30 min and the regeneration steps were carried out at 773 K during 6 h. The catalyst weight (0.500 g) used in these experiments was higher than that of the flow experiments in order to magnify the thermal effects during the reaction, the regeneration (carbon burn-off, a very exothermic reaction) and the reduction (an exothermic reaction) steps.

Temperature programmed reduction (TPR) experiments were carried out in a quartz flow reactor by using a 5% v/v H₂-N₂ reductive mixture (10 mL min⁻¹). The heating rate was 6 K min⁻¹. Before TPR experiments, samples were calcined *in situ* at 773 K during 3 h.

Temperature programmed oxidation (TPO) profiles of the used catalysts were determined by using the TGA technique. Experiments were carried out in a SDTA Mettler STARE equipment. Both the samples and references (fresh catalysts) were stabilized under flowing N₂ at 523 K before TGA experiments. TGA experiments were carried out by using 0.010 g of sample, with a heating rate of 5 K min⁻¹ from 523 to 773 K under flowing air.

3. Results and discussion

3.1. Characterization of the supports

The specific surface areas of MgAl₂O₄ and ZnAl₂O₄ (after purification) were: 37 m² g⁻¹ and 9.2 m² g⁻¹, respectively. The measured equilibrium pH value for MgAl₂O₄ was 8.4. This value was slightly lower than that reported in the literature [14] for MgAl₂O₄ with a remaining MgO content of 0.2 wt%. The isoelectric point reported in the literature [14] for ZnAl₂O₄ was about 8.0–8.2. According to Pakhomov and Buyanov [14], these supports can adsorb anionic species (like PtCl₆⁻), but the interaction between these spinels and PtCl₆⁻ are weaker than the PtCl₆⁻-Al₂O₃ interaction. Besides, the interaction strength of PtCl₆⁻ with the Zn spinel appears to be higher than for MgAl₂O₄ [14]. By considering that the metallic precursors used for the preparation of bimetallic catalysts were anionic ones in acidic media (H₂PtCl₆, and SnCl₂ stabilized in HCl), a good interaction of the metallic precursors with the surface of both supports can be expected.

Figure 1a shows the XRD spectrum obtained for the non-purified ZnAl₂O₄ sample. It can be observed a small amount of free ZnO. After the purification with (NH₄)₂CO₃, the characteristic XRD lines of ZnO were practically undetectable, and only the ZnAl₂O₄ structure was observed, such as it can be seen in figure 1b. In the case of MgAl₂O₄ (without purification) it was found, by comparing its spectrum (figure 2a) with those of pure MgO, γ -Al₂O₃ and MgAl₂O₄, that a given fraction of MgO and γ -Al₂O₃ remained in the samples. When purified, the XRD peaks due to MgO disappeared, remaining only small signals due to γ -Al₂O₃, but the main structure of the solid corresponded to MgAl₂O₄, as figure 2b shows.

3.2. Effect of the reaction temperature in *n*-butane dehydrogenation

According to the thermodynamic analysis [15], the *n*-butane dehydrogenation is an endothermic reaction. Hence, when the temperature increases the *n*-butane dehydrogenation is favored. Thus, the equilibrium conversion of *n*-butane (H₂/*n*-butane molar ratio = 4) into 1-butene is about 23% at 800 K. However, the hydrogenolytic capacity and the coke deposition also

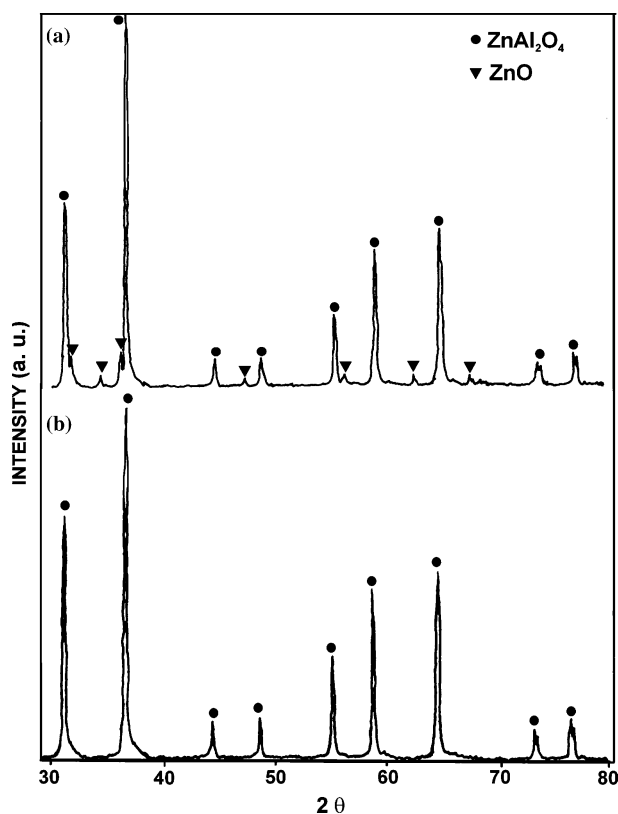


Figure 1. XRD spectra of non-purified ZnAl₂O₄ (a) and purified ZnAl₂O₄ (b).

increase at high reaction temperatures [16,17] leading to a lower efficiency of the process. In order to determine the effect of the reaction temperature on the activity, selectivity and catalyst deactivation, previous experiments were carried out in a continuous flow equipment at different reaction temperatures (773, 803 and 853 K), maintaining constant the other operating conditions.

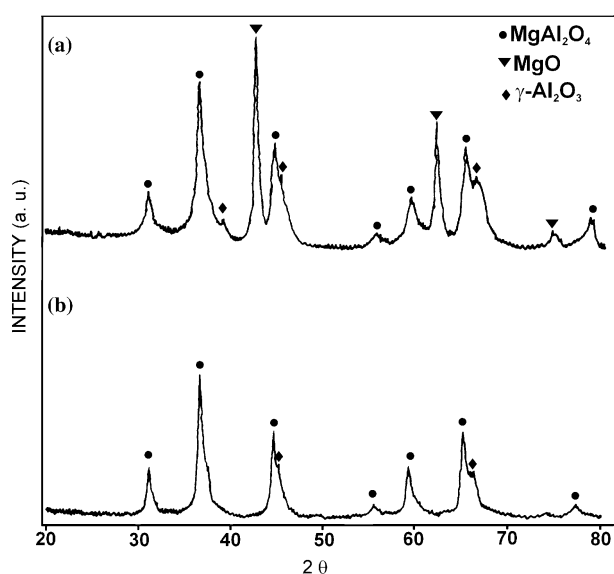


Figure 2. XRD spectra of non-purified MgAl₂O₄ (a) and purified MgAl₂O₄ (b).

Two catalysts were used for these experiments: PtSn(0.3 wt%)/ZnAl₂O₄ and PtSn(0.3 wt%)/MgAl₂O₄. Previous to the reaction, all catalyst samples were reduced *in situ* with H₂ at the same temperature as the reaction was carried out.

Figure 3 shows the initial values of *n*-butane conversion ($X^0_{n-C_4}$), measured at 10 min of the reaction time, as a function of the reaction temperature. Figure 4 displays the modification of the initial selectivity ($S^0_{BUTENES}$) to all butenes (1-butene, cis-2-butene, trans-2-butene and butadiene) with the reaction temperature. The deactivation parameter (defined as $\Delta X = 100(X^0 - X^f)/X^0$, where X^0 is the initial *n*-butane conversion and X^f is the final *n*-butane conversion measured at 120 min of the reaction time) is represented in figure 5 for the different catalysts as a function of the reaction temperature. It can be observed in figure 3 that the initial *n*-butane conversion increases with the reaction temperature, though this effect appears to be more pronounced for the bimetallic catalyst supported on

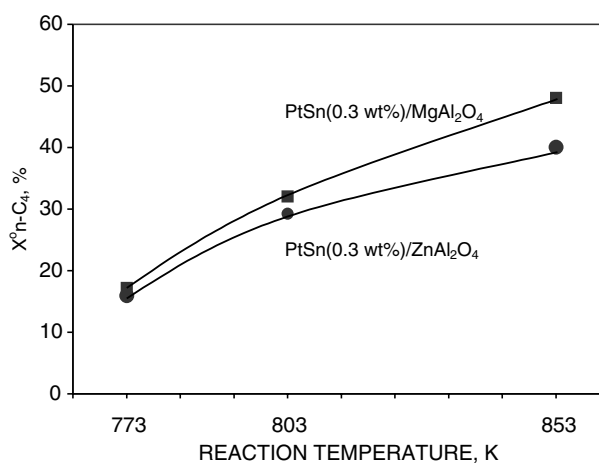


Figure 3. Effect of the reaction temperature on the initial *n*-butane conversion ($X^0_{n-C_4}$) for PtSn(0.3 wt%)/MgAl₂O₄ and PtSn(0.3 wt%)/ZnAl₂O₄ catalysts.

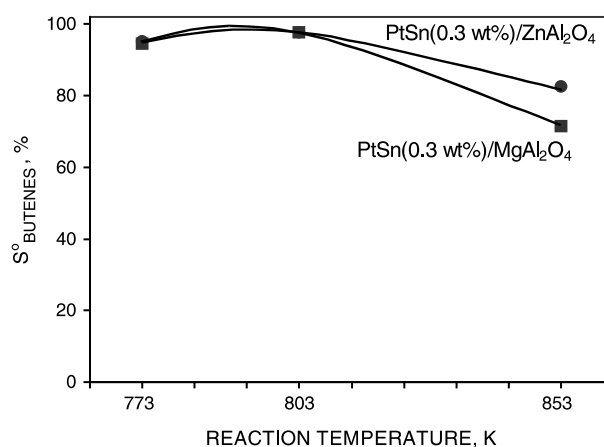


Figure 4. Effect of the reaction temperature on the initial selectivity to all butenes ($S^0_{BUTENES}$) for PtSn(0.3 wt%)/MgAl₂O₄ and PtSn(0.3 wt%)/ZnAl₂O₄ catalysts.

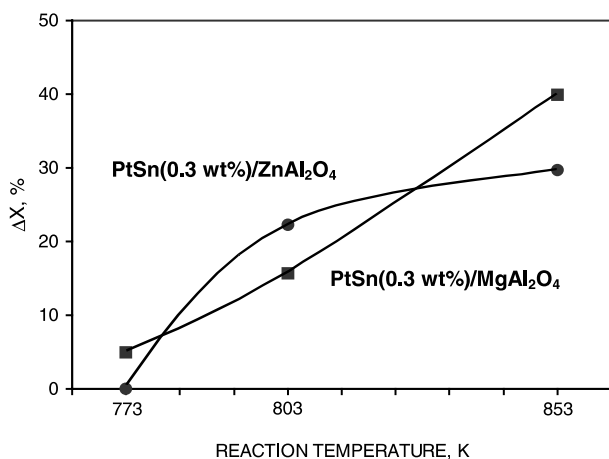


Figure 5. Effect of the reaction temperature on the deactivation parameter ($\Delta X = 100(X^0 - X^f)/X^0$, where X^0 and X^f are the initial and final *n*-butane conversion, respectively) for PtSn(0.3 wt%)/MgAl₂O₄ and PtSn(0.3 wt%)/ZnAl₂O₄ catalysts.

MgAl₂O₄ than for the PtSn/ZnAl₂O₄ catalyst. The initial selectivity to all butenes is similar for both catalysts series in the range of temperatures between 773 and 803 K, reaching values higher than 95%, but it decreases for higher reaction temperatures ($T > 803$ K), this effect being more pronounced for the bimetallic catalyst supported on MgAl₂O₄ than for the bimetallic one supported on ZnAl₂O₄, such as it can be seen in figure 4. This effect can be assigned to a higher formation of light paraffins (by hydrogenolysis) at high reaction temperatures. The deactivation parameter (ΔX) increases with the reaction temperature (figure 5). Thus, when the reaction temperature is 773 K the deactivation parameters have very low values, but the activity is also low for both catalysts. For reaction temperatures higher than 803 K, both the deactivation parameter and the catalytic activity increase, but the selectivity decreases, as figure 4 shows. From these results it can be concluded that good levels of *n*-butane conversion as well as a moderated deactivation and also high levels of selectivity to butenes can be obtained at 803 K. Hence, all experiments (both in continuous flow and pulse equipments) were carried out at 803 K in order to compare the behavior of catalysts with different Sn contents.

3.3. Test in a continuous flow equipment

Previous to the reaction all catalyst samples were reduced *in situ* at 803 K under flowing H₂ during 3 h. Figure 6a and b shows the values of the *n*-butane conversions (X_{n-C_4}) as a function of the reaction time for mono and bimetallic catalysts (with different Sn contents) supported on ZnAl₂O₄ and MgAl₂O₄, respectively. It must be indicated that the first point corresponds to 10 min of the reaction time. It can be observed in figure 6a that the Pt/ZnAl₂O₄ catalyst shows a low *n*-butane conversion (about 5–7%) and this value remains practically constant through the

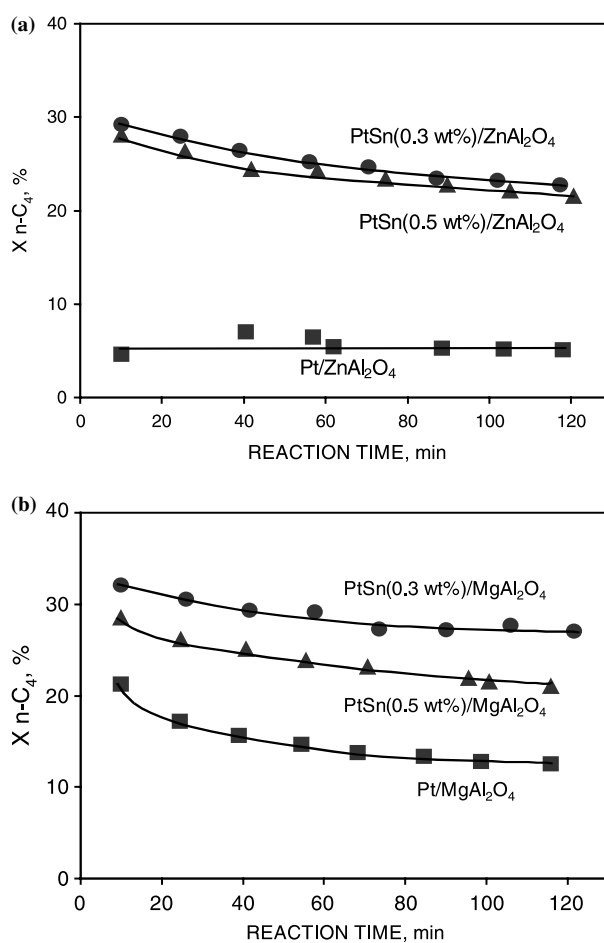


Figure 6. *n*-butane conversion (X_{n-C_4} , %) as a function of the reaction time for catalysts supported on ZnAl₂O₄ (a) and on MgAl₂O₄ (b) in flow experiments at 803 K.

reaction. According to figure 6b, the Pt/MgAl₂O₄ catalyst showed a higher initial conversion (20%) than the Pt/ZnAl₂O₄ one. When Sn is added to the Pt/ZnAl₂O₄ catalyst the initial activities sharply increase reaching values close to 30% for both Sn contents. In a similar way, the Sn addition to the Pt/MgAl₂O₄ catalyst increases the initial *n*-butane conversion reaching values of 29% for PtSn(0.5 wt%)/MgAl₂O₄ and 33% for PtSn(0.3 wt%)/MgAl₂O₄ samples.

Figure 7a and b shows the values of the selectivity to all butenes (S_{BUTENES}) as a function of the reaction time for mono and bimetallic catalysts supported on ZnAl₂O₄ and on MgAl₂O₄, respectively. It can be observed from these figures that the initial selectivity of the Pt/ZnAl₂O₄ catalyst is about 73%, and then it increases reaching a value of 90% at the final reaction time. In the case of the Pt/MgAl₂O₄ catalyst, the initial selectivity is about 77% and then it slightly increases up to a final value of 80% (figure 7b). When Sn is added to the Pt/ZnAl₂O₄ catalyst, the initial selectivity to butenes is close to 95% for 0.5 wt% of Sn and about 100% for 0.3 wt% Sn. These selectivity values are slightly modified through the reaction time. In the case of PtSn/MgAl₂O₄ catalysts

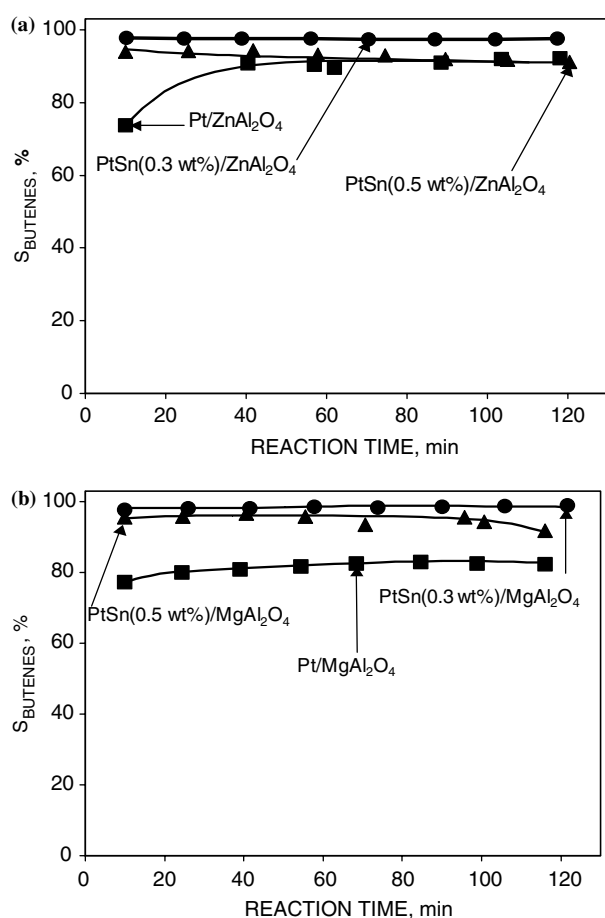


Figure 7. Selectivity to all butenes (S_{BUTENES}) as a function of the reaction time for catalysts supported on ZnAl_2O_4 (a) and MgAl_2O_4 (b) in flow experiments at 803 K.

(figure 7b), similar initial and final selectivity values to butenes (about 95–100%) were observed. It can be also noted that when the Sn loading increases from 0.30 up to 0.50 wt%, the effect on the selectivity to butenes is small for the bimetallic systems supported either on MgAl_2O_4 or ZnAl_2O_4 .

Figure 8 shows the parameter deactivation values for both catalysts series. It can be observed a very low deactivation parameter for the monometallic Pt/ ZnAl_2O_4 catalyst. However, this sample shows a very low initial activity (5–7%) and this activity is practically constant through the reaction. One probable explanation of this behavior can be related to that the major catalyst

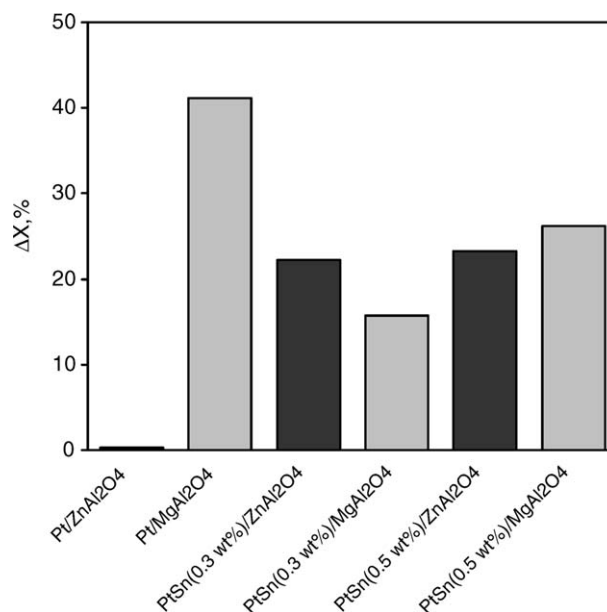


Figure 8. Deactivation parameter (ΔX : defined in the text) for different catalysts in flow experiments at 803 K.

deactivation by coke deposition could take place during the first minutes of the reaction (before the first sample taken at 10 min of the reaction time). This effect can be better explained at the light of the pulse experiment results, as it will be analyzed below. On the other hand, the Pt/ MgAl_2O_4 catalyst displays a very pronounced deactivation (about 41%). When Sn is added to the Pt/ MgAl_2O_4 catalyst, the deactivation parameter clearly decreases with respect to that of the monometallic one, mainly for a Sn content of 0.3 wt%. Figure 8 shows that PtSn(0.3 wt%)/ ZnAl_2O_4 and PtSn(0.5 wt%)/ ZnAl_2O_4 catalysts display similar deactivation parameter values (23–24%).

Table 1 shows the internal selectivity values to different butenes: 1-butene (S_1), trans- + cis-2 butenes (S_2) and butadiene ($S_{\text{butad.}}$) and the corresponding S_2/S_1 and $S_{\text{butad.}}/S_1$ ratios for the different catalysts. It must be indicated that the selectivities to different olefins do not change through the reaction time for all tested catalysts. Hence, the values indicated in table 1 are the average ones. It can be observed that 2-butenes are the main olefins, and that a small amount of butadiene was produced. However, the butadiene formation is higher for monometallic catalysts than for the corresponding

Table 1
Internal selectivity to different butenes (%). S_1 : 1-butene, S_2 : trans + cis-2 butenes, $S_{\text{butad.}}$: butadiene, for the different catalysts

Sample	S_1 , %	S_2 , %	$S_{\text{butad.}}$, %	S_2/S_1	$S_{\text{butad.}}/S_1$
Pt/ ZnAl_2O_4	29.3	65.2	5.5	2.22	0.188
PtSn (0.3 wt%)/ ZnAl_2O_4	29.2	69.0	1.8	2.36	0.062
PtSn (0.5 wt%)/ ZnAl_2O_4	29.8	68.5	1.7	2.30	0.057
Pt/ MgAl_2O_4	30.8	66.9	2.3	2.17	0.076
PtSn (0.3 wt%)/ MgAl_2O_4	28.1	70.4	1.5	2.50	0.053
PtSn (0.5 wt%)/ MgAl_2O_4	29.7	68.8	1.5	2.31	0.050

bimetallic ones. In fact, the $S_{\text{butad.}}/S_1$ ratio for the Pt/ZnAl₂O₄ catalyst was about three times higher than those corresponding to PtSn(0.3 wt%) and PtSn(0.5 wt%) catalysts supported on the same material, and this ratio for the Pt/MgAl₂O₄ catalyst was about 1.5 times higher than those corresponding to the bimetallic catalysts supported on MgAl₂O₄. These results would indicate that without a promotor addition (Sn), the sizes of the Pt ensembles are such as to allow the partial adsorption of butenes, and in consequence a second dehydrogenation step (to dienes) could take place. When an inert metal (like Sn) is added to Pt this effect appears to be decreased, which can be attributed to dilution, blocking or alloy formation effects [18]. According to Bhashin *et al.* [19], the dehydrogenation of olefins on platinum is faster than that of paraffins because the first ones interact more strongly with Pt than paraffins do. The modification of Pt by Sn addition would lead to a weaker interaction of the olefins [20] without affecting the paraffins-Pt interaction [19]. In this way the Sn addition to Pt inhibits the consecutive dehydrogenation of the mono-olefins without decreasing the paraffin dehydrogenation rate.

Moreover, it must be indicated that no skeletal isomerization was detected in our *n*-butane dehydrogenation experiments. This fact would indicate that the olefins produced on the metal surface are not isomerized on the support through a bifunctional mechanism, which requires a certain level of acidity in order to produce the skeletal isomerization [21]. This fact means that both supports used in this study show a very low acidic character.

3.4. Test in a pulse equipment

During these experiments, eight pulses of pure *n*-butane were injected on each sample. Results of the *n*-butane conversion as a function of the pulse number are indicated in figure 9a and b. It can be observed that both monometallic catalysts (Pt/ZnAl₂O₄ and Pt/MgAl₂O₄) display a high *n*-butane conversion after the first pulse. After the injection of four pulses of *n*-butane the deactivation is about 18% for the Pt/ZnAl₂O₄ catalyst versus 5% for Pt/MgAl₂O₄ catalyst (values referred to those corresponding to the first pulse), which indicates a faster initial deactivation for the monometallic catalyst supported on Zn/Al₂O₄.

It is worth noticing that the initial activities of the monometallic catalysts in flow experiments were clearly lower than those of the bimetallic ones, mainly for the Pt/ZnAl₂O₄ catalyst. On the other hand, the initial activities in pulse experiments (first pulse) of the monometallic catalysts are similar (for Pt/MgAl₂O₄) or slightly higher (for Pt/ZnAl₂O₄) than those for the corresponding bimetallic ones. The apparent increase of the initial activity for PtSn catalysts observed in flow experiments with respect to that of the monometallic

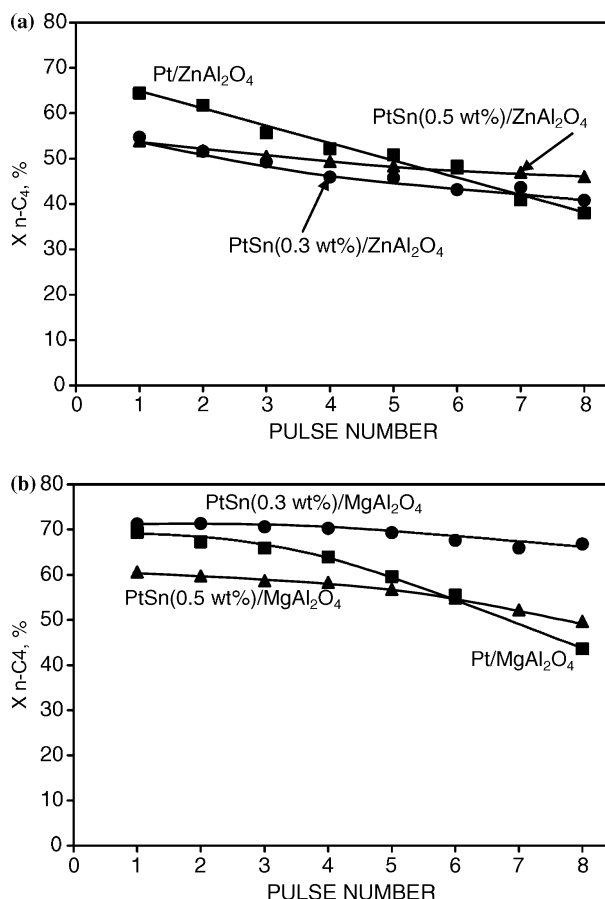


Figure 9. *n*-Butane conversion (X_{n-C_4} , %) as a function of the pulse number for catalysts supported on ZnAl₂O₄ (a) and on MgAl₂O₄ (b). Pulse experiments at 803 K.

ones can be explained by considering the results obtained in pulse experiments. In fact, the slopes of the conversion-pulse number curves at the eighth pulse (figure 9a and b) are clearly higher for monometallic catalysts than for bimetallic ones. This behavior can be related to the higher deactivation rate by coke deposition on the monometallic catalysts, as it will be discussed below.

In order to explain the different behavior of mono and bimetallic catalysts in flow and pulse experiments, the relative carbon retention (defined as the accumulative carbon amount deposited after the injection of *i* pulses and referred to the total carbon amount deposited on the corresponding monometallic catalyst after the injection of eight pulses) will be considered. figure 10a and b shows the relative carbon retention as a function of the pulse number for both catalyst series. It can be observed that the relative carbon retention after the injection of the first pulse is similar for both monometallic and bimetallic catalysts. However, the relative carbon retention after the injection of eight pulses of *n*-butane for monometallic catalysts are clearly higher than those for the corresponding bimetallic ones. It must be considered that the injection of the first pulse

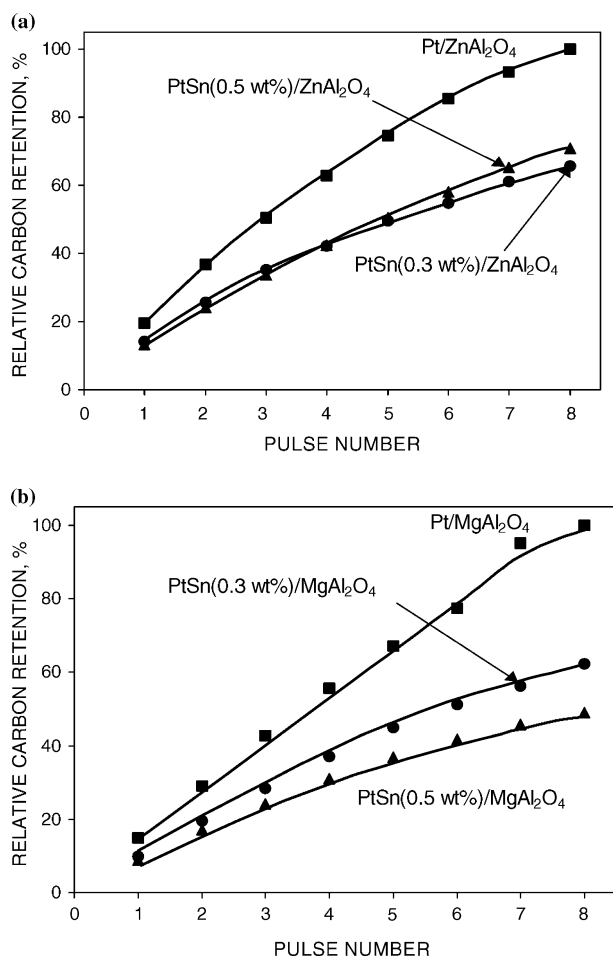


Figure 10. Accumulative relative carbon retention referred to that of the corresponding monometallic catalysts after the injection of eight pulses, (a) for catalysts supported on ZnAl₂O₄ and (b) for catalysts supported on MgAl₂O₄. Pulse experiments at 803 K.

of *n*-butane is produced on a clean surface (without carbon), while the first *n*-butane conversion point obtained in the flow experiment (at 10 min of the reaction time) corresponds to the reaction of *n*-butane on a partially deactivated surface which contained a given amount of carbon. In consequence, for a given catalyst it can be expected a higher activity after the injection of the first pulse of *n*-butane than that measured at 10 min of the reaction time in flow experiments.

Other point to be considered in the analysis of the results is related to the selectivity values shown in figure 11a and b. In a general way, the tendency is that the selectivity slowly increases as the pulse number increases, probably due to that the amount of carbon deposited on the catalysts is still low, and it has a small effect on the hydrogenolysis reaction (structure-sensitive reaction). In the case of bimetallic catalysts, the Sn addition to Pt leads to an increase of the selectivity to butenes with respect to the monometallic ones, mainly for catalysts supported on MgAl₂O₄. It can be also observed that after the eighth pulse the selectivity to

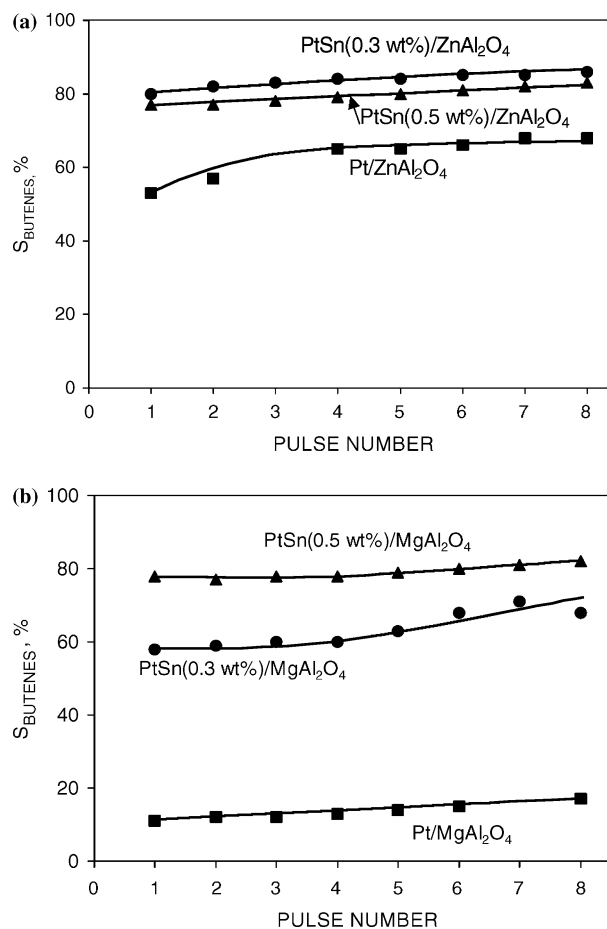


Figure 11. Selectivity to all butenes (*S*_{BUTENES}, %) as a function of the pulse number for catalysts supported on ZnAl₂O₄ (a) and for catalysts supported on MgAl₂O₄ (b). Pulse experiments at 803 K.

butenes tends to reach a similar value for both Sn contents in the two catalysts series. These results are in agreement with the selectivity results observed in flow experiments.

It must be noted that the Pt/ZnAl₂O₄ catalyst displays an important selectivity value to olefins for the first pulses, in contrast with the Pt/MgAl₂O₄ one which shows a very low selectivity to olefins (and in consequence a very important production of C₁–C₃ products) for the first pulses. These behaviors could be assigned to a very different hydrogenolytic capacity of these catalysts [20], probably related to a different structure of the metallic phase when the nature of the support is changed. It is known that the hydrogenolytic capacity is related to the concentration of big ensembles of Pt atoms, probably placed in corners or edges of the crystallites [22].

Another topic to be analyzed is the relationship between the catalyst deactivation and the coke amount. Figure 12 shows the *n*-butane conversion as a function of the absolute value of the carbon retention on monometallic samples. It can be observed a more

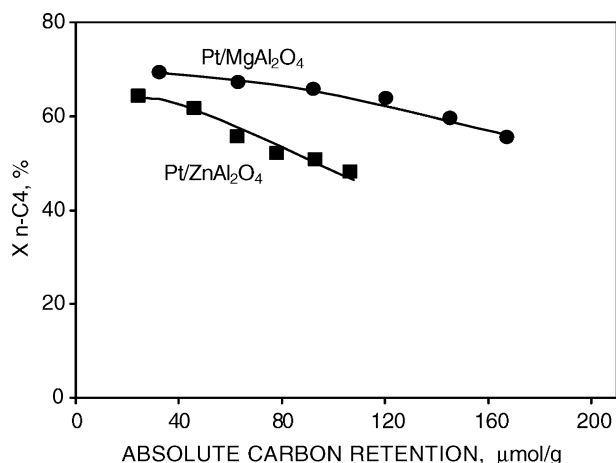


Figure 12. *n*-Butane conversion (X_{n-C_4} , %) as a function of the absolute carbon retention for Pt/ZnAl₂O₄ and Pt/MgAl₂O₄ catalysts. Pulse experiments at 803 K.

pronounced decay of the activity with the carbon retention for the Pt/ZnAl₂O₄ catalyst than for the Pt/MgAl₂O₄ one, even though the carbon amount deposited (after the injection of six pulses of *n*-butane) on the Pt/MgAl₂O₄ catalyst is higher than that deposited on Pt/ZnAl₂O₄. These results would indicate that a different toxicity and location of carbon can be expected for these two catalysts. In fact, it was reported in the literature that coke is more easily deposited on the planes than on corners and edges of the metallic crystallites [23,24]. From these evidences it can be inferred that a different concentration of corners and edges appears to exist in these two monometallic catalysts [20]. In addition, from these results (figures 10a, b and 12) it can also be considered that the catalyst deactivation through successive pulses could be linked to the carbon deposition and to its toxicity.

In order to determine the influence of the location and toxicity of the coke deposited on the catalysts, TPO

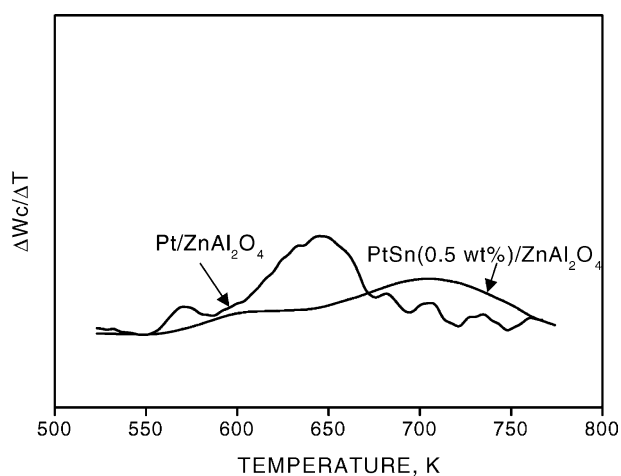


Figure 13. TPO profiles of used Pt and PtSn(0.5 wt%) catalysts supported on ZnAl₂O₄.

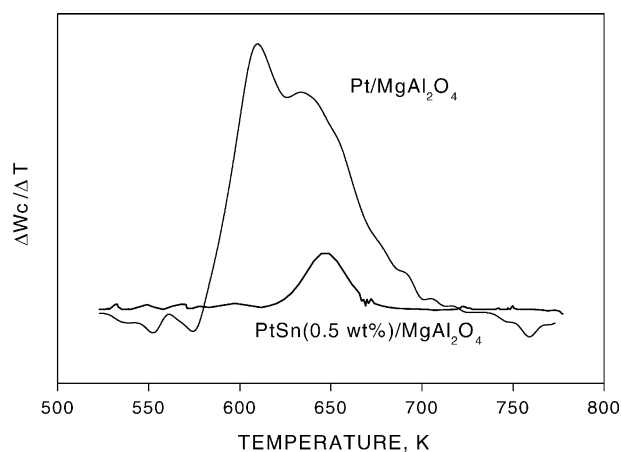


Figure 14. TPO profiles of used Pt and PtSn(0.5 wt%) catalysts supported on MgAl₂O₄.

measurements on coked samples after *n*-butane dehydrogenation in flow experiments were carried out. Figures 13 and 14 show the modification of $\Delta W_c/\Delta T$ (ΔW_c : weight loss due to carbon burn-off, ΔT : increment of temperature) as a function of the temperature. It can be observed for the Pt/ZnAl₂O₄ catalyst (figure 13) a main and broad peak at 648 K, the coke content (obtained by integration) being 0.42 wt%. In the case of the Pt/MgAl₂O₄ catalyst, the TPO profile shows a main and well defined peak at 609 K, and a shoulder at 638 K. In this case the coke content was 1.1 wt%. However, a higher amount of coke does not indicate a higher toxicity on the catalytic activity. In fact, figure 12 displays a higher deactivation for the Pt/ZnAl₂O₄ catalyst (where a lower coke amount is deposited) than for the Pt/MgAl₂O₄ one. It is probable that the coke deposited on the Pt/ZnAl₂O₄ catalyst, which is burned-off at a higher temperature than that deposited on the Pt/MgAl₂O₄ catalyst, would have a higher toxicity or polymerization degree. When Sn is added to monometallic catalysts, a different behavior was observed in both bimetallic samples. Thus, the addition of 0.5 wt% Sn to the Pt/ZnAl₂O₄ catalyst does not practically modify the amount of the deposited coke (it was detected 0.4 wt% C for the bimetallic one), but the TPO profile of the bimetallic catalyst displays a very broad peak with a maximum at higher temperatures (707 K), which could be assigned to carbon probably located in the metal-support interface having low toxicity. On other hand, when 0.5 wt% of Sn is added to the Pt/MgAl₂O₄ catalyst, the amount of the coke deposited on the catalyst sharply decreases (from 1.1 to 0.1 wt%) and the TPO profile shows only one and very small peak at 648 K. This coke appears to have a slightly higher toxicity than that deposited on the PtSn/ZnAl₂O₄ catalyst, according to the results showed in figure 8 (ΔX values for different catalyst), and it is probable that this coke could affect the metallic function.

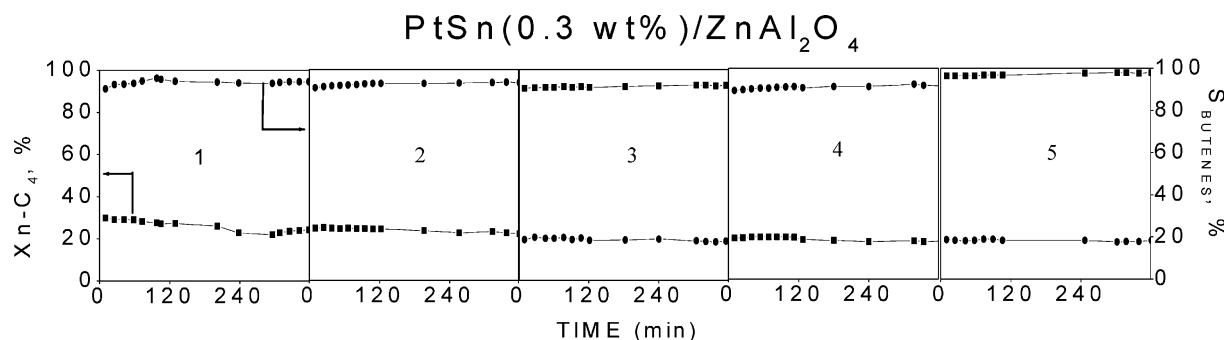


Figure 15. (■) *n*-Butane conversion (X_{n-C_4} , %) and (●) selectivity to butenes ($S_{BUTENES}$) as a function of the reaction time for the different reaction-regeneration cycles (1–5) corresponding to PtSn (0.3 wt%)/ZnAl₂O₄ catalyst. Reaction temperature: 803 K.

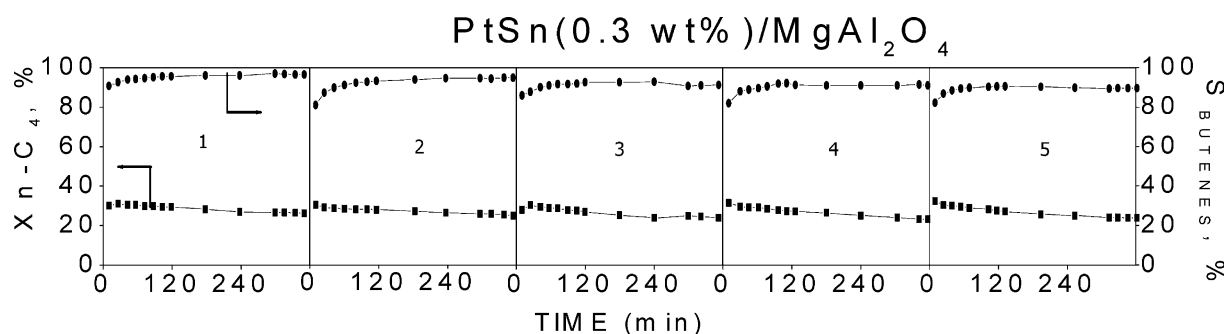


Figure 16. (■) *n*-Butane conversion (X_{n-C_4} , %) and (●) selectivity to butenes ($S_{BUTENES}$) as a function of the reaction time for the different reaction-regeneration cycles (1–5) corresponding to PtSn (0.3 wt%)/MgAl₂O₄ catalyst. Reaction temperature: 803 K.

3.5. Studies on the stability of PtSn (0.3 wt%)/ZnAl₂O₄ and PtSn(0.3 wt%)/MgAl₂O₄

Figures 15 and 16 display the modification of the activity (*n*-butane conversion) and selectivity to all butenes for PtSn(0.3 wt%)/ZnAl₂O₄ and for PtSn(0.3 wt%)/MgAl₂O₄ catalysts, respectively, through the five successive reaction-regeneration cycles.

From these figures it can be observed that the PtSn/MgAl₂O₄ catalyst showed a small modification of the initial activity between the first and the fifth cycle (2–3% referred to the first cycle). On the other hand, for the PtSn/ZnAl₂O₄ catalyst, the percentage of the decrease of the initial activity between the first and the fifth cycle (about 25% referred to the first cycle) was clearly higher than that for the PtSn/MgAl₂O₄ catalyst. Besides, the final activity value for the PtSn/MgAl₂O₄ catalyst series was higher than 20% for all cycles, while the final activity of PtSn/ZnAl₂O₄ decreased through the successive cycles, reaching a value of 16% for the fifth cycle.

Taking into account the selectivity values to all butenes (figures 15 and 16) it can be concluded that both PtSn/ZnAl₂O₄ and PtSn/MgAl₂O₄ catalysts display initial selectivity values (first cycle) around 90%. Besides, the initial selectivity to all butenes displays a low modification for the PtSn/ZnAl₂O₄ catalyst through the successive cycles. In the case of the PtSn/MgAl₂O₄ catalyst, it can be observed a decrease of the initial selectivity to butenes through the successive cycles (92% for the first cycle and 82% for the fifth cycle).

In order to obtain a better comparison of the performance of both catalysts, the initial and final yields to butenes for the different cycles were calculated as the product between the *n*-butane conversion and the selectivity to all butenes, and the results are shown in figure 17. It can be observed that the initial yield to butenes for the PtSn/MgAl₂O₄ catalyst shows a low modification through the successive cycles and that the final yield slowly decreases from 26% (first cycle) to 22% (fifth cycle). The results shown in figure 17 indicate that the yield to butenes for bimetallic catalysts supported on MgAl₂O₄ is clearly higher than for the bimetallic one supported on ZnAl₂O₄ through the successive cycles. In this sense the PtSn/ZnAl₂O₄ catalyst displays a diminution of both the initial yield (from 27% for the first cycle to 17% for the fifth cycle) and the final yield (from 22% for the first cycle to 16% for the fifth cycle).

Figures 18 and 19 show the TPR profiles of the PtSn/ZnAl₂O₄ and PtSn/MgAl₂O₄ catalysts after the cycles. Besides, the TPR profiles of the corresponding fresh samples are also included in these figures. In the case of the fresh PtSn/ZnAl₂O₄ sample, two peaks are observed: the main one at 561 K (probably due to the Pt and Sn co-reduction [20]), and the other one at 790 K, which could be assigned to segregated Sn species [20]. For the PtSn/ZnAl₂O₄ catalyst after the cycles, the TPR signals are very weak, with two reduction zones, one with a maximum at about 523 K and the other at 753 K. Pakhomov *et al.* [8] reported for the PtSn/ZnAl₂O₄

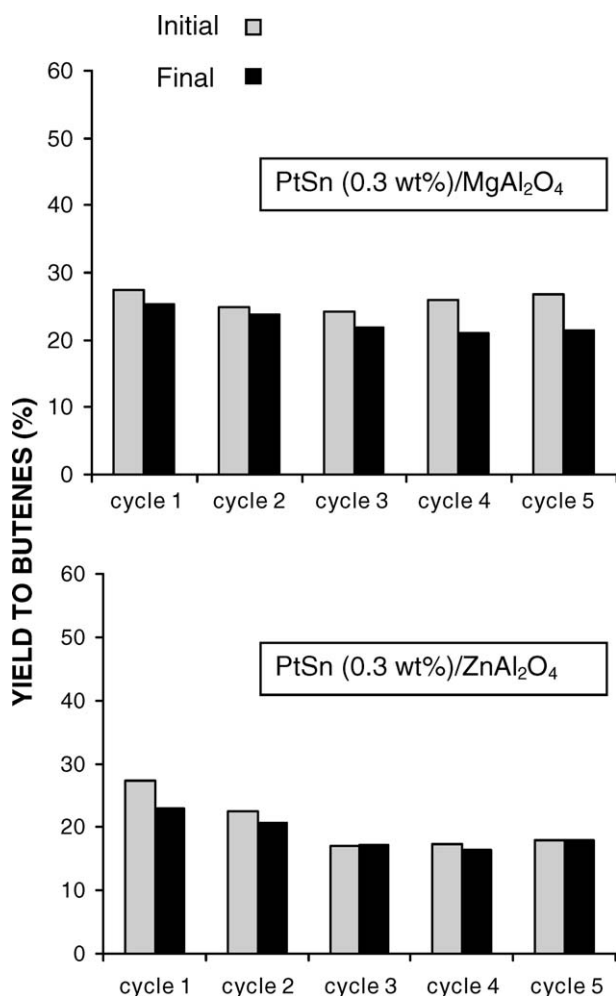


Figure 17. Initial (10 min of the reaction time) and final (360 min of the reaction time) yields to butenes corresponding to PtSn (0.3 wt%)/ZnAl₂O₄ and PtSn (0.3 wt%)/MgAl₂O₄ catalysts for different cycles. Reaction temperature: 803 K.

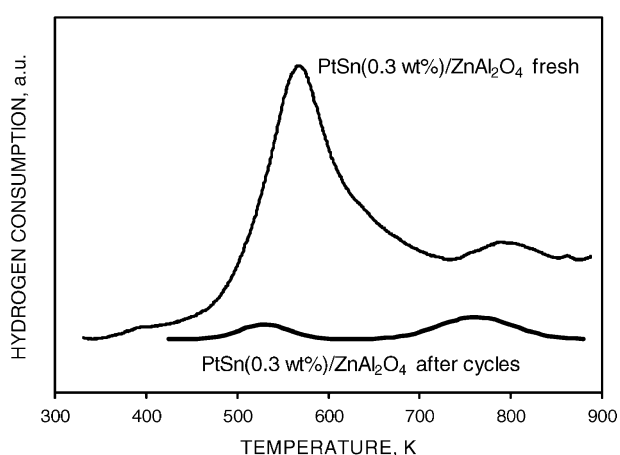


Figure 18. TPR profiles of PtSn (0.3 wt%)/ZnAl₂O₄ (fresh and after cycles) catalysts.

catalysts that an important fraction of metallic Pt is stabilized on the support after calcination in air. This can be the reason for the small TPR peak at low

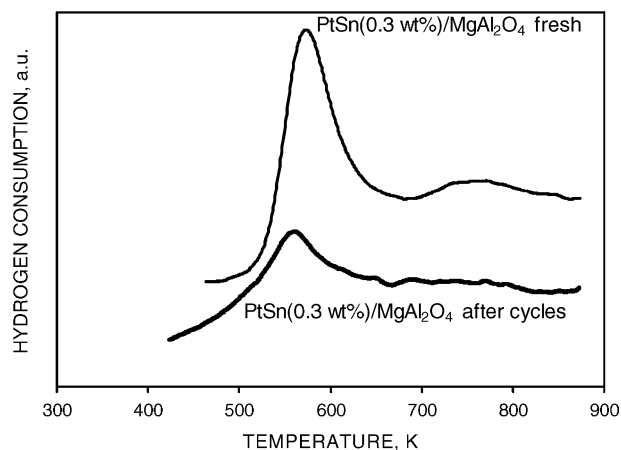


Figure 19. TPR profiles of PtSn (0.3 wt%)/MgAl₂O₄ (fresh and after cycles) catalysts.

temperature after the cycles. This means that an important fraction of metallic Pt would be stabilized on the support after the successive cycles and that the interaction between both metals appears to be decreased.

In the case of the TPR of the fresh PtSn/MgAl₂O₄ sample, it can be observed in figure 19 one important reduction peak at 566 K, probably due to the Pt and Sn co-reduction, and a small reduction zone between 650 and 850 K, which can be assigned to the reduction of Sn species stabilized on the support. After the cycles, the shape and position of the reduction peaks are very similar to those of the fresh sample, though with a lower magnitude. It must be indicated that no H₂ consumption was detected between room temperature and 400–450 K in both samples. The differences between the TPR profiles of bimetallic samples after the cycles can be related to a higher stability of PtSn/MgAl₂O₄ catalyst with respect to PtSn/ZnAl₂O₄ one through the successive reaction-regeneration cycles.

4. Conclusions

PtSn/ZnAl₂O₄ and PtSn/MgAl₂O₄ catalysts display a good activity and very high selectivity to all butenes at 803 K. For reaction temperatures lower than 803 K, the selectivity to butenes is very high, but the activity is very low, and in consequence the yield to olefins is low. For temperatures higher than 803 K the activity increases, but the selectivity to all butenes decreases and the deactivation parameter strongly increases.

The addition of different amounts of Sn (0.3 and 0.5 wt%) to monometallic catalysts increases both the initial activity and the selectivity to all butenes. It was found that the modification of the Sn content between 0.3 and 0.5 wt% in bimetallic catalysts on both supports is not an important factor for the catalytic behavior.

The catalyst deactivation appears to be related both to the coke deposition and the different toxicity and location of the coke on the catalyst surface, such as it is inferred from the results of the pulse and TPO experiments.

Bimetallic PtSn (0.3 wt%)/MgAl₂O₄ catalyst displays a higher stability through the successive reaction-regeneration cycles than the PtSn(0.3 wt%)/ZnAl₂O₄ sample. This different behavior can be related to a different effect of the reaction-regeneration cycles on the structure of the metallic phase, such as TPR results shows.

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