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Highly selective and stable bimetallic catalysts supported on different materials for *n*-butane dehydrogenation

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ABSTRACT

A study about the performance of Pt(0.3 wt%)Sn(0.3 wt%) catalysts supported on different materials in *n*-butane dehydrogenation is reported in this paper. The materials used as supports were γ-Al_2O_3, $ZnAl_2O_4$ spinel, $MgAl_2O_4$ spinel and spheres of α-Al_2O_3 with a washcoating of γ-Al_2O_3. The syntheses of both spinels leaded to very pure $ZnAl_2O_4$ and $MgAl_2O_4$ supports. The material prepared by washcoating showed the presence of an uniform and homogeneous layer of γ-Al_2O_3 (with a thickness between 12 and 18 μm) deposited on the spheres of α-Al_2O_3.

The best behavior in activity, selectivity and stability through five severe cycles was achieved by bimetallic PtSn catalysts supported on $MgAl_2O_4$ spinel and on the material prepared by washcoating. The very good performance of these catalysts through the different cycles of reaction-regeneration can be due to the presence of metallic phases which preserve the strong intermetallic interaction along the different treatments, thus avoiding segregation processes.

1. Introduction

The selective *n*-butane dehydrogenation to butenes is a very important industrial process since it produces a valuable raw material for the manufacture of different compounds (polybutenes, butene oxide, sec-butanol, methylethylacetone, acetic acid, maleic anhydride, butadiene, adipic acid, MTBE).

Paraffin dehydrogenation is an endothermic reaction that is limited by chemical equilibrium, so higher conversion will require higher reaction temperatures. In this sense, for 40% conversion, for example, the dehydrogenation of propane and butane requires temperatures of at least 853 and 803 K, respectively [1]. Production of light olefins by the catalytic dehydrogenation of light paraffins should maintain reasonable per-pass conversion levels and high olefin selectivity. Besides, this process would have to produce olefins in high yields over long periods of time without shutdowns.

This process can be carried out by using supported metallic catalysts, though several difficulties should be avoided in order to develop catalysts with a good performance. In this sense, both the inhibition of hydrogenolysis and cracking reactions and the minimization of coke deposition are major requirements in order to increase the selectivity to butenes and the catalytic stability. For this reason, the roles of the support and of the promoters added to the active metal (by example platinum) are keys for the better performance of the catalysts.

From the development of the STAR process [2], different bimetallic supported systems have been studied in this reaction. The use of non-acidic and thermal stable supports, such as alkali metal-doped gamma-alumina [3,4], different spinels [5–7], K-L-zeolite [8] and SiO_2 [9], appears as an important factor in order to inhibit undesirable reactions and to increase the stability of the metallic phase. Likewise, monolithic catalysts have acquired importance in the last years due to its advantages in the mass and heat transfer, particularly for fast reactions at high temperatures as steam reforming, dehydrogenation, oxydehydrogenation, etc. The washcoating is a very used method for depositing a layer of high surface-area oxide(s) in a low-surface area monolithic support. Active elements can be incorporated into the layer either during the washcoating step or after the washcoat for obtaining the catalyst. An adequate washcoating technique provide a thin and uniform layer with resistance to peeling and cracking in which the metals are deposited achieving good catalysts [10]. Besides, the addition of different promoters (such as Sn, Ga, In) to Pt [8,11–13] improves the catalytic behavior of the catalysts. Hence both the selection of an adequate support and the composition of the metallic phase can be considered as relevant factors in order to develop better catalysts for this process.

In this paper, the behavior of different bimetallic catalysts supported on γ-Al_2O_3, $ZnAl_2O_4$ spinel, $MgAl_2O_4$ spinel and spheres

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of α-Al_2O_3 with a washcoating of γ-Al_2O_3, in the *n*-butane dehydrogenation reaction through five successive cycles of reaction-regeneration is compared in order to obtain catalytic formulations with high yields to butenes and low deactivation by modifications of the metallic phase and coke formation.

2. Experimental

Different materials were used as supports of bimetallic catalysts: γ-Al_2O_3, $ZnAl_2O_4$, $MgAl_2O_4$, and spheres of α-Al_2O_3 with a γ-Al_2O_3 washcoating (Al_2O_3-wc). The γ-Al_2O_3 was a commercial one (CK-300 from Cyanamid Ketjen, $S_{BET} = 180\ m^2\ g^{-1}$), which was previously calcined in flowing air at 923 K during 3 h.

In order two synthesize both spinels ($ZnAl_2O_4$ and $MgAl_2O_4$), a solid reaction method proposed by Strohmeier and Hercules [14] was used. For $ZnAl_2O_4$, ZnO (99.9% from AnalarR) and γ-Al_2O_3 (99.9%) were the reactants, while for $MgAl_2O_4$, 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 for 72 h. At this temperature, the reaction between ZnO or MgO with alumina takes place. The solids thus obtained were ground to 35/80 mesh. In order to determine the formation of the respective $ZnAl_2O_4$ (or $MgAl_2O_4$), XRD spectra were obtained. The small amounts of MgO or ZnO remaining in these materials were eliminated by a purification treatment with aqueous solution of $(NH_4)_2CO_3$ 1 M (five washing steps with 1.5 ml solution/g 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 spectrometer with a Cu Kα radiation ($\lambda = 1.542$ Å), voltage: 30 kV and current: 30 mA. The surface area of $ZnAl_2O_4$ and $MgAl_2O_4$ were 10 and 40 $m^2\ g^{-1}$.

For the preparation of the support by washcoating, the starting materials were spheres (diameter = 2 mm) of a commercial α-Al_2O_3 ($S_g = 4.7\ m^2\ g^{-1}$), which were previously treated at room temperature with HCl 1N for 24 h (ratio of 1.4 cm^3 HCl/g α-Al_2O_3) in order to develop roughness in the external surface. Then the spheres were neutralized with NaOH (0.25N), followed by a drying step at 393 K for 12 h and a calcination in air at 773 K for 3 h in order to stabilize the structure. After this, a treatment with 2-propanol at 423 K (by injection of 2.5 cm^3 alcohol/h in a nitrogen stream of 300 $cm^3\ min^{-1}$) for 15 h was carried out to develop anchorage OH groups. Finally the spheres (modified with HCl and 2-propanol) were submitted to deposition processes of "primer" and "washcoating" of bohemite. For the deposition of "primer", the pretreated spheres of α-Al_2O_3 were submerged (with agitation) in a stable dispersion of a commercial bohemite (in a concentration of 20%, w/w) for 3 h, such as was proposed in the bibliography [15]. After the "primer" deposition, the "washcoating" was carried out for 3 h by using a stable dispersion (in nitric acid) of commercial bohemite using similar conditions. After the "primer" and "washcoating" deposition of bohemite, the spheres were dried in flowing air at 323 K and then calcined in air at 773 K for 3 h in order to transform the bohemite phase into γ-Al_2O_3. The specific surface area corresponding to the layer of γ-Al_2O_3 deposited on the external surface of the spheres was about 180 $m^2\ g^{-1}$. These supports were impregnated with solutions of LiOH and NaOH, such as to obtain concentrations of 0.13 wt% Li and 0.17 wt% Na, that poison the acidic sites of the alumina.

In order to determine the uniformity of the layer deposited by washcoating, a characterization by scanning electronic microscope (SEM), with a JSM-35C, JEOL model, equipped with SemAfore digital image acquisition system were done. The samples were coated by a thin layer of gold to give them conductivity before the observation.

Specific surface areas of the supports were determined in a Quantachrome Corporation NOVA-1000 surface area analyzer, by using N_2 as an adsorbate.

Isopropanol dehydration experiments at atmospheric pressure were carried out in a continuous flow reactor in order to determine the acid behavior of the different supports. Prior to the reaction, samples were reduced "in situ" with H_2 at 773 K. 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 473 K.

Bimetallic Pt(0.3 wt%)Sn(0.3 wt%) catalysts were prepared by successive impregnation of the corresponding support with an aqueous solution of H_2PtCl_6, dried and then impregnated with a hydrochloric solution (1.2 M HCl) of $SnCl_2$. In both cases the impregnations were carried out a room temperature during 6 h. After impregnation, samples were dried at 383 K during 12 h, and calcined in air at 773 K. In all cases the impregnating volume/support weight ratios were 1.4 ml g^{-1}, and the concentrations of the impregnation solutions were the corresponding to obtain the desired Pt and Sn contents. Besides, the monometallic Pt (0.3 wt%) catalysts were also prepared by impregnation of the corresponding support with an aqueous solution of H_2PtCl_6, followed by similar thermal treatments to those of bimetallic samples.

The following catalysts were used for this study: Pt/Al_2O_3, PtSn/Al_2O_3, PtSn/$ZnAl_2O_4$, PtSn/$MgAl_2O_4$ and PtSn/Al_2O_3-wc (catalyst supported on spheres of α-Al_2O_3 with a γ-Al_2O_3 washcoating). In all cases the Pt and Sn contents were 0.3 wt%.

TPR experiments were performed in a quartz flow reactor. The samples were heated at 6 K min^{-1} from room temperature up to about 973 K. 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 773 K for 3 h.

The different catalysts were tested in the *n*-butane dehydrogenation reaction in a continuous flow reactor at 803 K. The experiments were performed in a quartz 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, residence time = 0.025 g cat. min (mL *n*-butane)$^{-1}$). The reactive mixture was prepared "in situ" by using mass flowmeter controllers. All reactive gases and N_2 (used for purge) and H_2 (used for the previous reduction of catalysts) were high purity ones (>99.99%). The reactor effluent was analyzed by a GC-FID equipment. The chromatographic column (1/8 in. × 6 m) used for these analyses was a packed one (20% BMEA on Chromosorb P-AW 60/80). The column was maintained at 323 K during the analysis experiments. With this analytical device methane, ethane, propane, propylene, *n*-butane, 1-butene, 2-cis-butene, 2-trans-butene and 1–3 butadiene can be detected. The *n*-butane conversion was calculated as the ratio between the sum of the chromatographic areas of all reaction products (except H_2) affected by the corresponding response factor and the chromatographic area of non-reacted *n*-butane affected by its response factor. The selectivity to different reaction products was defined as the ratio: mol of product/Σmol of all products (except H_2). Taking into account the high temperatures used for the reaction, 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) at 803 K. Results showed that a negligible *n*-butane conversion was obtained (<1%). Hence the participation of the homogeneous phase reaction can be discarded at this reaction temperature.

Besides the above-mentioned test in *n*-butane dehydrogenation, studies on the catalytic stability of the bimetallic PtSn catalysts supported on the different supports 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 N_2, regeneration by using an O_2–N_2 (5%, v/v O_2) mixture, purge with N_2, and reduction with H_2 at 803 K. This sequence was repeated five times. The purge steps with N_2 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.

Carbon contents of the different 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

Fig. 1 shows X-ray diffractograms of both synthesized Zn and Mg spinels, thus displaying only the diffraction lines corresponding to $ZnAl_2O_4$ and $MgAl_2O_4$, respectively.

In order to determine the uniformity of the layer of γ-Al_2O_3 deposited by washcoating on the spheres of α-Al_2O_3 (γ-Al_2O_3-wc), a characterization by scanning electronic microscope (SEM) were done. Fig. 2 shows two photographies of a calcined sample with deposition of "primer" and "washcoating". Fig. 2a shows a sphere with an uniform coating, while Fig. 2b displays a sectional view with a good homogeneity of the deposited layer. It was observed that the thickness of the γ-Al_2O_3 coating ranged between 12 and 18 μm.

In order to determine the acid–base properties of the different supports, the different materials were evaluated in the 2-propanol dehydration reaction, which is carried out on acid sites. It is known that the commercial gamma-alumina has Lewis acid sites [16] which can catalyze the 2-propanol dehydration reaction [17], and the initial dehydration conversion of γ-Al_2O_3 reached about 25%. For the other supports ($ZnAl_2O_4$, $MgAl_2O_4$ and γ-Al_2O_3-wc) the dehydration conversions were practically negligible (<1%), which indicate the very low acidic characteristics of these materials. Besides, experiments of 2-propanol dehydration were carried out on all PtSn catalysts supported on the different materials in order to determine the possible influence of the low Cl contents incorporated during the impregnation of the metallic precursors. These bimetallic catalysts did not show differences in dehydration conversion with respect to the pure supports, thus indicating that low chlorine contents do not modify the acidic characteristics of these materials.

Table 1 shows the catalytic behavior (initial – X^0 – and final – X^f – n-butane conversions, initial and final selectivities to butenes, initial and final yields, and a deactivation parameter – ΔX, defined as: 100. $X^0 - X^f/X^0$ – that takes into account the activity fall along the reaction time) of the different bimetallic catalysts supported on the different materials. Besides, results for the supported monometallic catalysts (as reference) are displayed in the same table. In general, supported monometallic Pt catalysts show poor results in dehydrogenation of light paraffins. The Pt/$ZnAl_2O_4$ catalyst shows the lowest conversion, and this fact is probably due to the diffusion of Zn in the spinel net forming a Pt–Zn alloy, which is inactive for dehydrogenation. This alloy is destroyed when the Sn is added for obtaining bimetallic catalyst, thus increasing clearly the activity [18]. The performance of monometallic Pt catalysts supported on

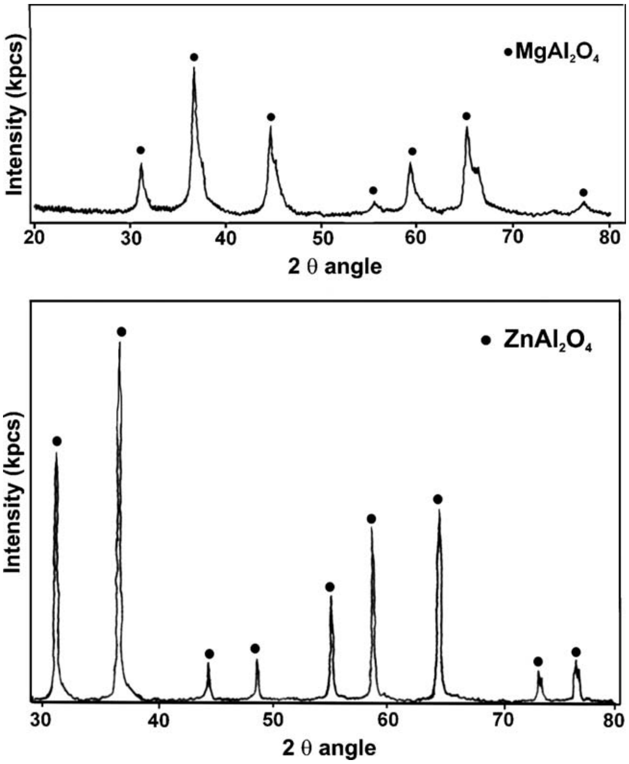

Fig. 1. XRD measurements of purified $MgAl_2O_4$ and $ZnAl_2O_4$, synthesized by the solid reaction method.

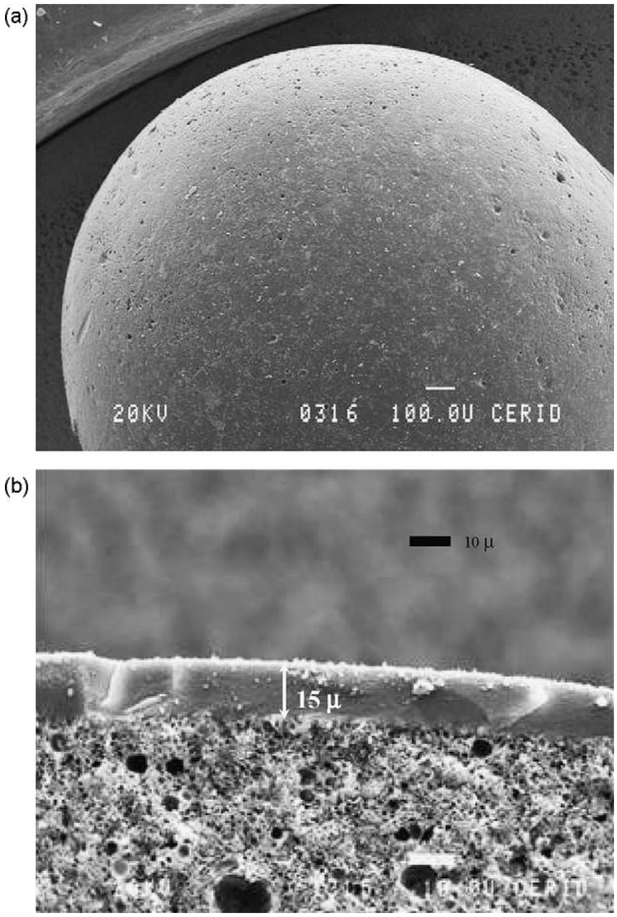

Fig. 2. SEM microphotographies of the layer of γ-Al_2O_3 deposited by washcoating on the spheres of α-Al_2O_3: (a) top view and (b) sectional view.

Table 1

Results of *n*-butane dehydrogenation in flow experiments. Carbon concentration (*C*) determined after the reaction experiments.

Catalysts	X_0[a], %	X_f[b], %	S_0[c], %	S_f[d], %	ΔX[e], %	Y_0[f], %	Y_f[g], %	*C*, wt%
Pt/Al_2O_3	45	10	53	50	78	24	5	6.5
Pt/Al_2O_3-wc	29	17	60	59	41	17	10	0.5
$Pt/ZnAl_2O_4$	5	5	74	92	0	4	5	0.4
$Pt/MgAl_2O_4$	21	12	77	82	41	17	10	1.1
$PtSn/Al_2O_3$	43	13	78	86	70	34	11	4.2
$PtSn/Al_2O_3$-wc	29	28	96	96	4	28	27	0.3
$PtSn/ZnAl_2O_4$	29	23	98	98	22	29	22	0.4
$PtSn/MgAl_2O_4$	32	27	98	99	16	31	27	0.2

[a] Initial *n*-butane conversion (measured at 10 min of the reaction time).

[b] Final *n*-butane conversion (measured at 120 min of the reaction time).

[c] Initial selectivity to all butenes (measured at 10 min of the reaction time).

[d] Final selectivity to all butenes (measured at 120 min of the reaction time).

[e] $100(X^0 - X^f)/X^0$.

[f] Initial yield to all butenes (calculated as the product of the conversion and the selectivity to all butenes).

[g] Final yield to all butenes (calculated as the product of the conversion and the selectivity to all butenes).

an acidic support like γ-Al_2O_3 was also not good, such as Table 1 shows. The presence of acid sites in this support catalyzes undesirable reactions like hydrogenolysis and cracking and coke formation, thus producing gases (such as methane, ethane, ethylene, propane and propylene), decreasing the selectivity to the different butenes, and increasing the deactivation parameter (ΔX) due mainly to the carbon deposition. In this sense Table 1 shows the important carbon content (6.5%) of Pt/Al_2O_3 after the reaction experiment.

The addition of a second metal, like Sn, to Pt produces important modifications in the catalytic performance. In fact, Table 1 shows that the tin addition to Pt/Al_2O_3 produces an important increase of the final selectivity to butenes from 50 to 86%. This important increase of the dehydrogenation selectivity goes parallel to a pronounced decrease of the hydrogenolytic activity, since lower amounts of light gases (C_1, C_2 and C_3 compounds) were produced. Besides, a decrease of the carbon formation and of the deactivation parameter is also observed in Table 1.

Besides PtSn catalyst supported on the material prepared by washcoating ($PtSn/Al_2O_3$-wc) shows not only high activities and selectivities to butenes, but also the lowest deactivation parameter ($\Delta X = 3.5\%$), since the *n*-butane conversion remains practically constant along the 2 h of reaction time. This fact is in agreement with the low carbon deposition of this bimetallic catalyst, of only 0.25 wt% (Table 1).

Tin addition to Pt supported on the two spinels ($ZnAl_2O_4$ and $MgAl_2O_4$) increases in a pronounced way both the activity and the selectivity to butenes (about 100%). With respect to the stability of these bimetallic samples, a different behavior was observed in both bimetallic samples. Thus, the addition of 0.3 wt% Sn to the $Pt/ZnAl_2O_4$ catalyst does not practically modify the amount of the deposited coke (it was detected 0.40 and 0.42 wt% C for the bimetallic and monometallic catalyst, respectively). This fact is due to that the monometallic sample shows a very low activity and hence it produces a low coke formation during the reaction experiment. On the other hand the bimetallic catalyst supported on $ZnAl_2O_4$ increases the conversion approximately six times (as it was above explained) and however, the carbon formation remains unchanged, with respect to the monometallic $Pt/ZnAl_2O_4$. Besides, when 0.3 wt% of Sn is added to the $Pt/MgAl_2O_4$ catalyst, the deactivation parameter decreases (from 41.3 to 15.9%) and the amount of the coke deposited on the catalyst sharply decreases (from 1.1 to 0.2 wt%).

In conclusion, the Sn addition to Pt/Al_2O_3-wc, $Pt/ZnAl_2O_4$ and $Pt/MgAl_2O_4$ leads to an important increase of the selectivity values to all butenes (1-butene, *cis*- and *trans*-2-butenes, and 1,3-butadiene), a decrease of the deactivation parameter values and to a lower carbon formation. This fact could be due to that the presence of Sn in the vicinity of Pt would produce a decrease both of the size of the Pt ensembles and of the Pt-olefin interaction strength, by geometric and electronic effects. Therefore, once the olefin is formed (from the paraffin dehydrogenation) it is immediately desorbed, avoiding the formation of the coke precursors by a further dehydrogenation reaction on the bimetallic catalyst [7].

Apart from the above mentioned test in *n*-butane dehydrogenation, studies on the catalytic stability of the monometallic Pt/Al_2O_3 and $Pt/MgAl_2O_4$ and bimetallic $PtSn/Al_2O_3$, $PtSn/Al_2O_3$-wc, PtSn(0.3 wt%)/$ZnAl_2O_4$ and PtSn(0.3 wt%)/$MgAl_2O_4$ catalysts were carried out. These stability tests consisted on five reaction-regeneration cycles. In order to obtain a better comparison of the performance of the different 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 Figs. 3–5.

For monometallic catalysts (Fig. 3), Pt/Al_2O_3 shows a very low stability of the metallic phase, since it displays an important decrease of yield in each cycle and along the five cycles. On the other hand, the differences between the initial and final yield of each cycle for $Pt/MgAl_2O_4$ catalyst are low compared to those for Pt/Al_2O_3. Besides, for the monometallic catalysts supported on $MgAl_2O_4$, there is a negligible fall in the yields along the cycles. These results show the influence of the support on the stability of Pt.

For bimetallic catalysts, the worst stability behavior of the metallic phase was for $PtSn/Al_2O_3$ catalyst, which displayed an initial conversion and selectivity to butenes (in the first cycle) of 53% and 43%, respectively, and a final conversion and selectivity (in the fifth cycle) of 15% and 83%, respectively. The evolution of the yields to butenes of this $PtSn/Al_2O_3$ catalyst (Fig. 4) shows an important fall through the different reaction-regeneration cycles.

On the other hand, the behavior of $PtSn/Al_2O_3$-wc along the five cycles was very good, since this catalyst displayed an initial conversion and selectivity to butenes (in the first cycle) of 31% and 98%, respectively, and a final conversion and selectivity (in the fifth cycle) of 21% and 96%, respectively. The evolution of the yields to butenes of this sample (Fig. 4) shows an important stability of the metallic phase through the successive reaction-regeneration cycles. It can be observed in Fig. 4 that the initial yield to butenes for the $PtSn/Al_2O_3$-wc catalyst shows a low modification through the successive cycles and that the final yield slowly decreases from the first to the fifth cycle. The results shown in Fig. 4 indicate that the yields to butenes for bimetallic catalysts supported on the support prepared by washcoating are clearly higher than for the

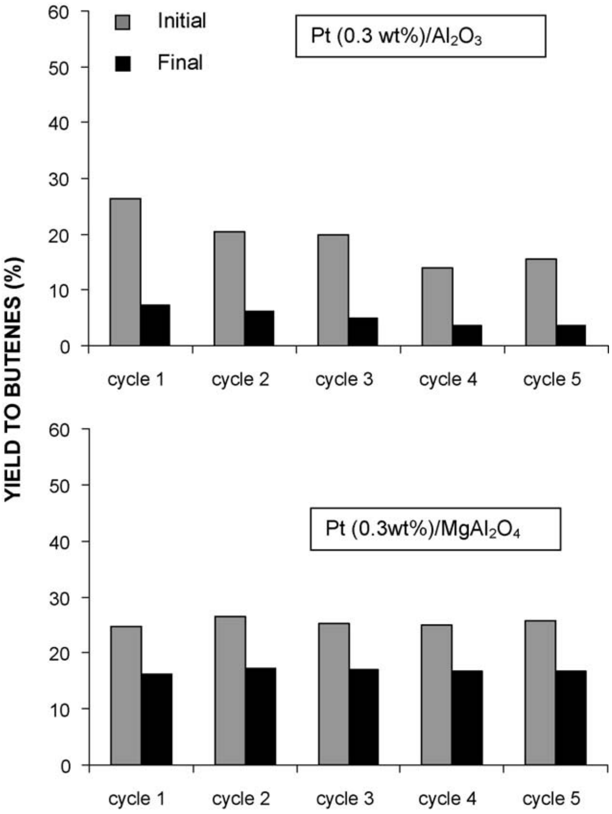

Fig. 3. Initial (10 min of the reaction time) and final (360 min of the reaction time) yields to butenes corresponding to Pt/Al_2O_3 and Pt/$MgAl_2O_4$ catalysts for different cycles.

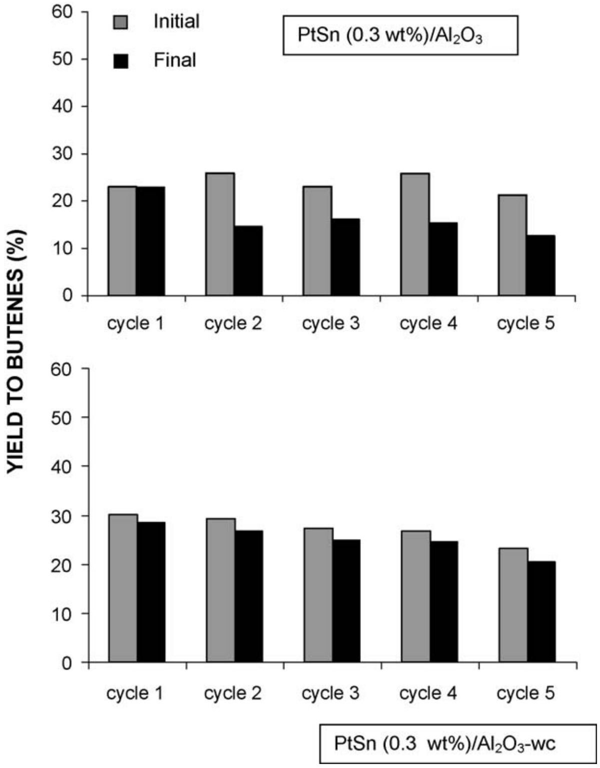

Fig. 4. Initial (10 min of the reaction time) and final (360 min of the reaction time) yields to butenes corresponding to PtSn/Al_2O_3 and PtSn/Al_2O_3-wc catalysts for different cycles.

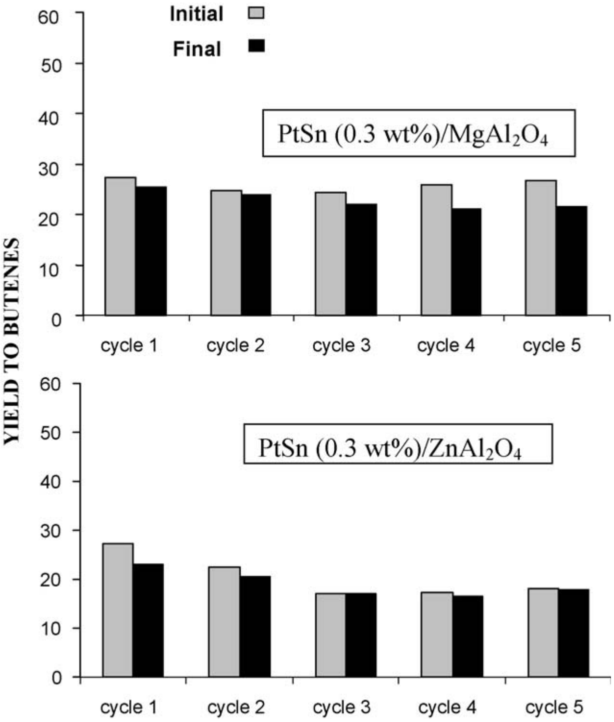

Fig. 5. Initial (10 min of the reaction time) and final (360 min of the reaction time) yields to butenes corresponding to PtSn/$MgAl_2O_4$ and PtSn/$ZnAl_2O_4$ catalysts for the different cycles.

bimetallic one supported on Al_2O_3 along the successive cycles. In this sense the PtSn/Al_2O_3 catalyst displays a diminution of the final yield to butenes (from 23% for the first cycle to 12% for the fifth cycle).

With respect to the catalysts supported on both spinels, the stability of the metallic phase of PtSn supported on $MgAl_2O_4$ is different from that of PtSn/$ZnAl_2O_4$ catalyst. In this sense, the first catalyst (PtSn/$MgAl_2O_4$) 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/$ZnAl_2O_4$ 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/$MgAl_2O_4$ catalyst. Besides, the final activity value for the PtSn/$MgAl_2O_4$ catalyst series was higher than 22% for all cycles, while the final activity of PtSn/$ZnAl_2O_4$ decreased through the successive cycles, reaching a value of 16% for the fifth cycle. Taking into account the selectivity values to all butenes it can be concluded that both PtSn/$ZnAl_2O_4$ and PtSn/$MgAl_2O_4$ catalysts display initial selectivity values (first cycle) around 90%, and final selectivities (fifth cycle) of 95% and 90%, respectively. It can be observed in Fig. 5 that the initial yield to butenes for the PtSn/$MgAl_2O_4$ 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 Fig. 5 indicate that the yield to butenes for bimetallic catalysts supported on $MgAl_2O_4$ is clearly higher than for the bimetallic one supported on $ZnAl_2O_4$ through the successive cycles. In this sense the PtSn/$ZnAl_2O_4$ 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).

In conclusion, the best catalysts in activity, selectivity and stability through five severe cycles are those supported on $MgAl_2O_4$ spinel and on the support prepared by washcoating (Al_2O_3-wc). Other authors have studied the influence of the

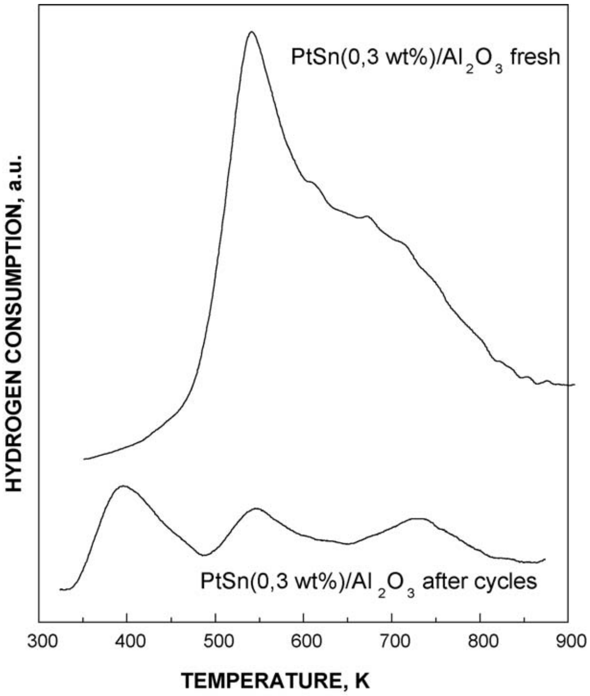

Fig. 6. TPR profiles of PtSn (0.3 wt%)/Al_2O_3 (fresh and after cycles) catalysts.

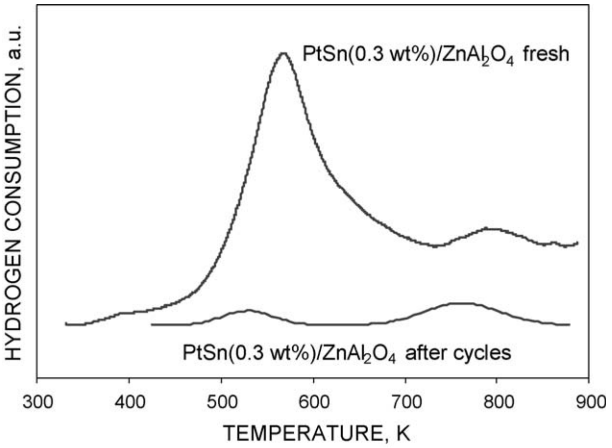

Fig. 8. TPR profiles of PtSn (0.3 wt%)/$ZnAl_2O_4$ (fresh and after cycles) catalysts.

support, such as SiO_2 and MgO, on the catalytic behavior of PtSn catalysts for paraffins dehydrogenation. In this sense, Llorca et al. [19] found that MgO supported bimetallic catalysts were more selective to isobutenes than the catalysts supported on SiO_2 and Al_2O_3. These catalysts also show higher deactivation values along seven hours of reaction time than PtSn/MgO catalysts, both in presence and absence of H_2.

The behavior of these catalysts through the different cycles of reaction-regeneration can be correlated with the probable modification of the metallic phase, which was characterized by temperature programmed reduction. In this sense Figs. 6–9 show the TPR profiles of the PtSn/Al_2O_3, PtSn/Al_2O_3-wc, PtSn/$ZnAl_2O_4$ and PtSn/$MgAl_2O_4$ catalysts, respectively, both before the cycles (fresh sample) and after the cycles.

Fig. 6 shows that the fresh PtSn/γ-Al_2O_3 catalyst displays a main reduction peak at 542 K, and a shoulder at higher temperatures, between 600 and 800 K. The main peak would correspond to the co-reduction of Pt species (probably oxy- or hydroxychlorined [20]) and Sn, which would be interacting or forming a bimetallic phase, while the reduction zone at higher temperatures would correspond to the reduction of free Sn species [21]. On the other hand, in PtSn/Al_2O_3 catalyst, submitted to the successive reaction-regeneration cycles, besides the two reduction zones previously mentioned (which are much lower than those of the fresh sample), another peak at low temperatures appears. This new peak at 394 K would correspond to the reduction of PtO_2, such as it was identified by Borgna et al. [20], and it would be due to Pt segregation from the bimetallic phase, process that occurred during the reaction-regeneration cycles. The lower height of the peak corresponding to the PtSn co-reduction in the catalysts submitted to cycles could be due to the difficulty to oxidize the PtSn alloys during the calcinations treatment previous to the TPR experiment, though the existence of a sinterization process of the metallic phase cannot be discarded.

For the PtSn catalyst supported on the material prepared by washcoating (Al_2O_3-wc), the fresh one shows a broad TPR peak with a maximum at 580 K, characteristic of an important PtSn co-reduction probably due to strong intermetallic interactions, such as Fig. 7 shows. After the severe reaction-regeneration cycles, the main peak becomes broader and smaller, and it is shifted to lower temperatures (with the maximum at 555 K). However, no reduction zones at temperatures of very low temperatures (400 K), characteristic of segregated PtO_2, appear. This important

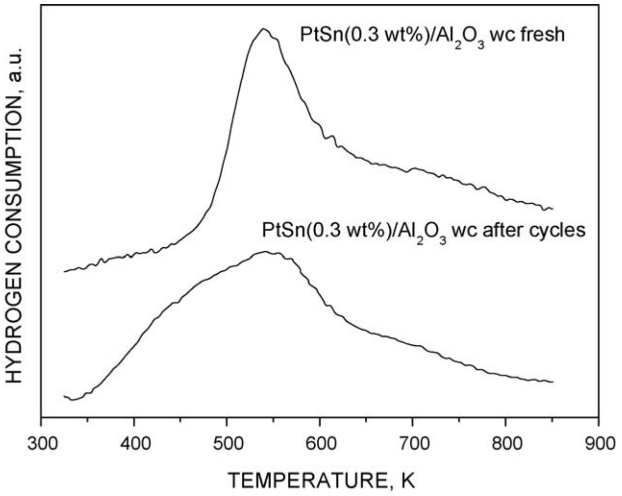

Fig. 7. TPR profiles of PtSn (0.3 wt%)/Al_2O_3-wc (fresh and after cycles) catalysts.

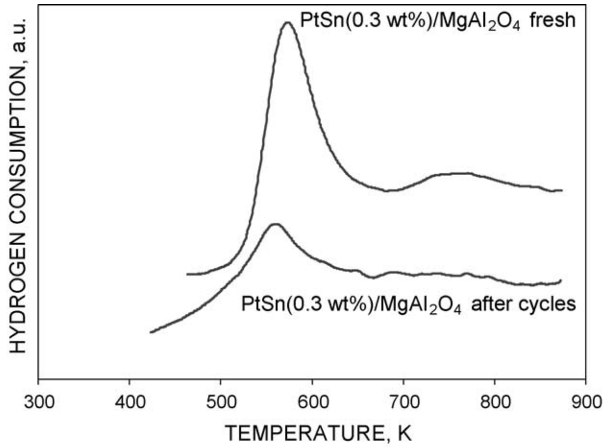

Fig. 9. TPR profiles of PtSn (0.3 wt%)/$MgAl_2O_4$ (fresh and after cycles) catalysts.

difference in the state of the metallic phase of the PtSn/Al_2O_3-wc with respect to the PtSn/Al_2O_3 catalysts, would be responsible for the better catalytic behavior through the successive reaction-regeneration cycles.

In the case of the fresh PtSn/$ZnAl_2O_4$ sample, two TPR peaks are observed in Fig. 8, the main one at 561 K (probably due to the Pt and Sn co-reduction), and the other one at 790 K, which could be assigned to free Sn species [21]. For the PtSn/$ZnAl_2O_4$ 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. In this case it is not observed the peak due to the PtO_2 reduction at very low temperatures. Pakhomov et al. [22] reported for the PtSn/$ZnAl_2O_4$ 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 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/$MgAl_2O_4$ sample, it can be observed in Fig. 9 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 H_2 consumption was detected between room temperature and 400–450 K in both samples. The differences between the TPR profiles of bimetallic samples supported on spinels after the cycles can be related to a higher stability of PtSn/$MgAl_2O_4$ catalyst with respect to PtSn/$ZnAl_2O_4$ one through the successive reaction-regeneration cycles.

In conclusion, with respect to the TPR profiles of the fresh catalysts supported on the different materials, they show similar aspects, with a main reduction peak between 540 and 580 K and a small reduction zone at higher temperatures. The quantification of consumed hydrogen from TPR experiments of the fresh catalysts were done. All fresh bimetallic PtSn catalysts displays a H_2 consumption between 45 and 60 μmol H_2 g cat^{-1}. Considering that all Pt is completely reduced, the percentages of tin reduced from Sn(IV) to Sn(0) ranges between 30 and 55%. These results are in agreement with XPS ones shown in the literature for PtSn catalysts, which displayed the presence of Sn(0) together with oxidized Sn [4,23]. In all fresh catalysts, an important fraction of tin would be as zerovalent tin, probably forming PtSn alloys, and the other fraction as oxidized Sn species stabilized on the support. This strong PtSn interaction observed in TPR of fresh bimetallic catalysts would cause the very good catalytic behavior of PtSn catalysts supported on $MgAl_2O_4$, $ZnAl_2O_4$ and Al_2O_3-wc. Considering the fresh PtSn/Al_2O_3 catalyst, which also shows a good metallic interaction, the bad catalytic performance (high deactivation parameter and coke formation, and poor selectivity) would be due to the acidity of the γ-Al_2O_3. With respect to the TPR results of the catalysts after cycles, the quantification of consumed hydrogen is not valid due to the initial state of the metals after the cycles (before the TPR) is unknown. This is due to the difficulty to oxidize the PtSn alloys during the calcination treatment previous to the TPR experiment after cycles, which produce a very low hydrogen consumption.

4. Conclusions

Three different materials which can be used as supports of catalysts for light paraffins dehydrogenation have been synthesized: two spinels of $ZnAl_2O_4$ and $MgAl_2O_4$, and a novel support consisting of α-Al_2O_3 spheres with a washcoating of γ-Al_2O_3.

The best behavior in activity, selectivity and stability through five severe cycles was achieved by bimetallic PtSn catalysts supported on $MgAl_2O_4$ spinel and on the material prepared by washcoating. The very good performance of these catalysts through the different cycles of reaction-regeneration can be due to metallic phases which preserve the strong intermetallic interaction along the different treatments, thus avoiding segregation processes.

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