n-Decane dehydrogenation on Pt, PtSn and PtGe supported on spinels prepared by different methods of synthesis

Adriana D. Ballarini*, Sergio R. de Miguel, Alberto A. Castro, Osvaldo A. Scelza

Instituto de Investigaciones en Catálisis y Petroquímica (INCAPE), Facultad de Ingeniería Química (Universidad Nacional del Litoral)-CONICET, Santiago del Estero 2654, 3000AJO Santa Fe, Argentina

1. Introduction

Olefins are very important raw materials in the petrochemical and petroleum refining industries due to their applications in several processes. One application of α-monoolefins of high molecular weight is in the production of biodegradable detergents or tensoactives. This industry has become very important as well, since dodecylbenzene was found to have better properties than soaps. These detergents were initially produced by alkylation of benzene with tetramers of propene (a mixture of C10–C12 highly branched olefins) followed by sulfonation and neutralization with NaOH. This process had the problem of the lack of biodegradability of the detergents [1,2]. A new process that appeared in the mid 60s, was the production of sodium alkylbenzenesulfonate. This compound has an aliphatic linear chain of C10–C14 [3,4] which allows a fast biodegradation. These biodegradable detergents are obtained by alkylation of benzene with linear α-monoolefins of C10–C14. The production of the biodetergents at industrial scale was successful, thus displacing the preceding technologies. In this way the production of linear alkylbenzene or linear alkylbenzene sulfonate (LAB or LABS) increased significantly [3,4].

This paper studies the production of 1-decene from the n-decane catalytic dehydrogenation. The dehydrogenation of high paraffins to the corresponding n-monoolefins can take place on noble metals (Group 10) like Pt. This reaction is normally accompanied by undesirable side ones such as hydrogenolysis, cracking, aromatization and coke formation. In consequence, it is very important to analyze the addition of modifiers (elements of the Group 14 like Sn and Ge), which can affect the activity, selectivity and stability of the catalysts [3–10]. Furthermore the coke deposition can be diminished by using H2 in the feed [11]. In the present paper monometallic (Pt) and bimetallic (PtSn and PtGe) catalysts supported on ZnAl2O4 obtained by both mechanochemical synthesis (MS) or coprecipitation (COPR) are evaluated in the n-decane dehydrogenation. The specific surface area of ZnAl2O4 can be improved choosing the appropriate synthesis method. In general, there are several preparation methods of ZnAl2O4 spinels, for example solid state-reaction or ceramic method [12–19] or wet chemical routes such as precipitation or coprecipitation [12–14,20–24], sol–gel [12–14,25–28] and other methodologies like hydrothermal methods [29–33], combustion in aqueous solution [34], molten salts synthesis [35], etc. These techniques try to reduce the severity of the thermal treatments, thus achieving a material of higher specific area and higher chemical purity. It must be noted that the comparison of the catalytic behavior of monometallic catalysts supported on the ZnAl2O4 spinel prepared by COPR, MS and ceramic method (CM) was previously reported in the bibliography by Ballarini et al. [36]. The Pt catalysts prepared with ZnAl2O4 COPR presented better activity and selectivity (in the reaction of n-butane dehydrogenation) than the ones prepared with ZnAl2O4 MS and ZnAl2O4 CM, and this could be correlated with a higher metallic dispersion and lower particle sizes, detected by H2 chemisorption and TEM, respectively. For this
reason, in this paper, ZnAl2O4 prepared by mechanochemical synthesis and coprecipitation was used as support of metallic catalysts for paraffin dehydrogenation.

With reference to this topic, there are no papers in the open literature about bimetallic catalysts supported on ZnAl2O4 for n-decane dehydrogenation, specially the use of couples composed of Pt and Ge on these supports. It must be remembered that ZnAl2O4 has a spinel structure which is appropriated for this reaction type due to the high thermal stability, neutral acid-base characteristic and low Pt sintering rate since there is a strong metal–support interaction [37–39]. Bhasin et al. [40] studied that the unmodified alumina-supported platinum catalysts are highly active but not selective to dehydrogenation. They showed a simple reaction scheme for light paraffins dehydrogenation, but the complexity of the reaction increases when the number of C atoms in the reactant increases.

In this paper the effect of the Sn or Ge loading added to Pt is also studied, in order to correlate the properties of the support with the physicochemical characteristics of the catalysts and the catalytic properties.

2. Experimental

In the mechanochemical synthesis of the ZnAl2O4 (MS), γ-Al2O3 (CK 300, 99.9% from Cyanamid Ketjen) and ZnO (AnalaR, 99.7%) were ground until fine powder and they were mixed in a stoichiometric ratio. Then distilled water was added in order to produce a paste. The paste was ground by using a grinder that consists of a teflon® cylinder of 140 mL and zirconia balls with a diameter of 13 mm. The cylinder rotated at 200 rpm in contact with air at room temperature for 12 h. The paste thus obtained was dried at 120 °C and calcined at 900 °C for 12 h. After the precursor of ZnAl2O4, a purification step was achieved by washing the precursors with (NH4)2CO3 1 M to eliminate residues of ZnO. The ratio volumen of solution/mass of solid was 1.5 mL/g.

ZnAl2O4 COPR was prepared by coprecipitation of the two metallic ions (Zn and Al) at variable pH. The precipitation was made by using Al(NO3)3 9H2O, Baker, 98.9% and Zn(NO3)2 6H2O, Baker, 99.0%. Finally the pH was adjusted at 7.5 by using a NH4(OH) 50% (v/v). After precipitation under stirring at 50 °C a gel is obtained.

The 2-propanol dehydration reaction (used for the measure-}

sion of the support (10 mL water g of support−1) was performed following the technique reported by Román-Martínez et al. [41]. The suspension was stirred and the pH was measured until it reached the constant value.

The monometallic Pt (0.3 wt.%) catalyst was prepared by impregnation (6 h, 25 °C) of the corresponding support (ZnAl2O4 MS and ZnAl2O4 COPR) with an aqueous solution of H2PtCl6 (Aldrich 98%). The concentration of the H2PtCl6 solution was such as to obtain the desired Pt loading. The impregnating volume/support weight ratio was 1 mL g−1 for ZnAl2O4 MS and 0.7 mL g−1 for ZnAl2O4 COPR. After 6 h, the samples were dried at 120 °C for 12 h and calcined in air at 500 °C for 3 h.

Bimetallic PtSn catalysts were obtained by impregnation of the monometallic Pt catalyst (previously dried) with a SnCl2 solution (in an HCl 1.2 M medium). In all the cases the Pt concentration was 0.3 wt.% The Sn concentrations in the impregnating solutions were 0.0253 and 0.042 mol L−1 for Sn 0.3 and 0.5 wt.% loading, respectively. After impregnation with Sn, samples were dried at 120 °C for 12 h.

Bimetallic Pt-Ge catalysts were also obtained by impregnation of the monometallic Pt catalyst (previously dried) with an aqueous solution of GeCl4 (dissolved in HCl 1M). The Pt concentration in the catalysts was 0.3 wt.% The Ge concentrations in the impregnating solutions were 0.025 and 0.04 mol L−1 for the Ge loading of 0.18 and 0.3 wt.%, respectively. After impregnation with Ge the samples were dried at 120 °C for 12 h. Finally bimetallic samples were calcined at 500 °C for 3 h under flowing air.

TPR experiments of the catalysts were carried out at atmospheric pressure and using a reductive mixture of H2–N2 (5% H2 v/v, 10 cm3 STP min−1), and a heating linear programming rate of the sample (0.300 g) equal to 6 k min−1 from room temperature up to 700 °C. Before the TPR measurements the samples were calcined “in situ” at 500 °C with flowing air 160 min−1 g−1 cat−1 for 3 h.

The H2 chemisorption was performed at 25 °C in a static volumetric equipment. The sample used in the experiments ranged between 0.300 and 0.500 g. In these experiments the catalysts were previously reduced in H2 at 500 °C for 2 h, then passed under high vacuum (10−5 Torr) at the same temperature for 2 h and finally cooled down to room temperature. The H2 adsorption isotherms were performed at room temperature between 0 and 100 Torr. The isotherms were linear in the range of used pressures and the H2 chemisorption capacity was calculated by extrapolation of the isotherms to zero pressure.

The cyclohexane (CH) dehydrogenation reaction was carried out in a differential flow reactor fed at 6 mL h−1 with a H2 – CH mixture (H2/CH molar ratio = 26). Previous to the reaction the catalysts were reduced “in situ” under flowing H2 at 500 °C for 3 h at the reaction temperature indicated in each case. The reaction products were analyzed by GC using a Chromosorb column at 60 °C. The activation energies were obtained from the slope of the curve ln Rh v s 1/T (– temperature, K). Rh was calculated from the conversion obtained at three different temperatures. The sample mass was chosen to obtain a conversion less than 5%, condition in which the reactor can be considered as a differential one. For the cyclopentane (CP) hydrogenolysis reaction, the catalyst samples were previously reduced “in situ” under flowing H2 at 500 °C for 3 h. The reaction was performed in a differential flow reactor fed at 6 mL h−1 with H2 – CP mixture (H2/CP molar ratio = 26). The reaction temperature was 500 °C. The reaction products were analyzed by GC using a Chromosorb column at 25 °C.

The XPS spectra were obtained in a spectrometer Specs, by using MgKα or AlKα (for Ge determination at high BE) sources at 1253.6 or 1486.6 eV, respectively. Other conditions were: power of 100 W (10 kV and 10 mA) and the pressure of the analysis chamber was 4.10−10 Torr. Before XPS, samples were previously reduced in H2 at 530 °C for 3 h. The BE were referred to the Al2p peak (74 eV). Spectra were obtained by using the Specslab software. The peak areas
were estimated by means of a combination of Lorentzian-Gaussians curves in a different proportion and using Casa XPS software.

Transmission electron micrographs of the reduced catalysts were taken by using a JEOL 100CX microscope with a nominal resolution of 6 Å, operated with an acceleration voltage of 100 kV, and magnification ranges of 80,000× and 100,000×. The specimens were introduced into the microscope column. For each catalyst, a very important number of Pt particles were observed and the distribution curves of particle sizes were done.

To quantify the carbonaceous deposits, the profiles of temperature-programmed oxidation before and after the n-decane dehydrogenation reaction were determined using the thermogravimetric analysis (TGA) technique. The experiments were carried out on the SDTA Mettler STARe. Fresh (used as a reference) and used catalysts were stabilized under N₂ flow at 250 °C for 1 h before starting the TPO experiments. The samples (0.010 g) were heated at 5 °C min⁻¹ from 250 to 500 °C under air flow.

The n-decane dehydrogenation reaction was carried out in a flow reactor. The reactive mixture (n-C₁₀-H₂) is prepared “in situ” in the desired proportion by using a mass flow control for H₂ and a Sage syringe pump for n-C₁₀. This mixture was vaporized before injected to the reactor. All the gases were high purity (99.95% minimum) ones. The liquid effluent obtained by condensation of the outlet of the reactor was analyzed in a Varian STAR 3400 CX chromatograph with a FID detector and a capillary column CP-Sil-PONA CB, 50 m length, 0.2 mm diameter and 0.5 μm of the film thickness. The working temperature of the column was 250 °C.

In order to determine the conversion and selectivity values, fractions of the liquid product were sampled at 10 min of the reaction beginning and then at intervals of 15 min until 130 min of total reaction time. By using the chromatographic analysis, five groups of compounds were identified according to the retention time:

- (1) Light paraffins of C₅-C₁₀ from the cracking reactions, [<C₁₀].
- (2) n-decane (used as reference peak), [n-C₁₀].
- (3) 1-decene or α-monoolefins of C₁₀, [1-C₁₀ = a].
- (4) Others monoolefins (positional isomers) and conjugated diolefins and not conjugated, n-dienes, n-trienes, [C₁₀=] (except 1-decene).
- (5) Non linear chains including ramified chains, isoparaffins, isoolefins, cyclization products, aromatics, alkyl aromatics, etc., [i-C₁₀].

It must be indicated that in all cases the liquid yield (<C₁₀) was in the range of 97–98%. In previous experiments it was found that a feeding of a mixture of n-decane and hydrogen with a H₂/n-C₁₀H₂2 = 4-6 molar ratio decreased the catalyst deactivation that allows the reaction evolution to be controlled. Other operating conditions were: T = 465 °C, P = 1 atm, LHSV (h⁻¹) = 40 and weight of catalyst = 0.35 g.

The n-decane conversion was calculated as the sum of the percentages of the chromatographic areas of all the reaction products affected by the corresponding response factors, except for H₂.

The selectivities to different group of products (j) were defined as follows:

\[ S_j = \frac{\text{mol product}_j}{\Sigma \text{mol product}} \] \text{(except H}_2)\text{. }

The yield to 1-decene was defined as:

\[ Y_{1\text{-decene}} = \text{conversion} \times \text{selectivity to 1-decene} \].

Conversions, selectivities and yields were calculated at different reaction times (10–130 min). It is worth noticing that even though the catalysts were tested at conversions between 2 and 13%, no important selectivity changes were obtained at different conversions.

### 3. Results and discussion

#### 3.1. Characterization of supports

Table 1 shows the results of specific surface area (SBET) and pore volume of ZnAl₂O₄ prepared by different methods.

<table>
<thead>
<tr>
<th>Method</th>
<th>SBET (m² g⁻¹)</th>
<th>V_pore (ml g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS</td>
<td>21</td>
<td>0.053</td>
</tr>
<tr>
<td>COPR</td>
<td>40</td>
<td>0.118</td>
</tr>
</tbody>
</table>

![Fig. 1. XRD of the ZnAl₂O₄ obtained by coprecipitation. (a) Precursor and (b) precursor calcined at 800 °C.](image)

#### Table 1

Specific surface area (SBET) and pore volume of ZnAl₂O₄ prepared by different methods.
all cases the reaction produces propylene. It must be noted that γ-Al₂O₃ has Lewis acidity [43] and subsequently the 2-propanol conversion is high (about 20%). With reference to ZnAl₂O₄ samples, they show a lower dehydration capacity, evidenced by the low acidity of these supports. However ZnAl₂O₄ COPR shows a slightly higher conversion than ZnAl₂O₄ MS, and consequently the last sample has the lowest acidity.

Equilibrium pHs of the spinels obtained by different methods were 8.2–8.6; these values being in agreement with the very low acid character [44] of the supports according to the dehydration of 2-propanol reaction results.

3.2. Characterization of the metallic phase

Tables 2 and 3 show initial rate (R_CH) and activation energy values for cyclohexane dehydrogenation reaction at 400 °C (structure-insensitive reaction [45,46]) and also initial reaction values from cyclopentane hydrogenolysis reaction (R_CP) at 500 °C (structure sensitive reaction) [47–49] for Pt, PtSn and PtGe catalysts supported on ZnAl₂O₄ MS and ZnAl₂O₄ COPR. When a second metal is added to a Pt catalyst, two effects can take place, viz, the geometric one, this being the blocking and/or dilution of the Pt active atoms by the second metal, and the electronic one that modifies the electronic structure of the Pt. It can be observed from Tables 2 and 3 that monometallic catalysts supported on ZnAl₂O₄ MS and ZnAl₂O₄ COPR show similar activation energy values. The Sn or Ge addition increases the activation energy, this indicating a certain electronic modification of the metallic phase probably by alloy formation. This electronic effect seems to be more pronounced for Sn containing catalysts than Ge containing ones when ZnAl₂O₄ MS is used as support. For ZnAl₂O₄ COPR series there are small differences in the activation energies. Besides, the second metal addition decreases R_CH values in about one order of magnitude. It can be concluded that the addition of either Sn or Ge to Pt/ZnAl₂O₄ catalysts decreases the dehydrogenation activities thus showing a blocking geometric effect by Sn or Ge that decreases the number of exposed Pt atoms and also electronic effects as it was above mentioned.

On the other hand, the cyclopentane hydrogenolysis reaction is influenced by the size and structure of the metallic particles. Besides a special arrangement of surface active atoms are needed for this reaction to take place [50]. Results of this reaction are shown in Tables 2 and 3. Monometallic catalysts supported on both ZnAl₂O₄ supports show hydrogenolytic activities only from 500 °C so it could be explained that these supports produce metallic structures with low density of edges and corners (active centers for this reaction) [21,51]. In bimetallic catalysts supported on ZnAl₂O₄ MS or ZnAl₂O₄ COPR the second metal addition inhibits the hydrogenolytic reaction. This can be due not only to an electronic modification of Pt by Sn or Ge but also geometric effects. Sn or Ge addition decreases the concentration of metallic ensembles that the cyclopentane hydrogenolysis needs. Summarizing the results of both test reactions, the second metal introduces both geometric and electronic modifications in the metallic phase.

Fig. 4a and b shows the TPR profiles of PtSn (0.3 and 0.5 wt.%) catalysts supported on ZnAl₂O₄ MS and ZnAl₂O₄ COPR. Monometallic Pt and Sn catalysts are also added for comparison. Fig. 5 shows the TPR profiles of PtGe (0.18 and 0.3 wt.%) catalysts supported on ZnAl₂O₄ MS (a) and ZnAl₂O₄ COPR (b). The profiles of the monometallic catalysts are also included. Zinc aluminate is not reduced in the used range of temperature (25–700 °C) [14]. Fig. 4a shows that the Pt/ZnAl₂O₄ MS catalyst gives a well-defined reduction peak at 260 °C, whereas the corresponding peak of Pt/ZnAl₂O₄ COPR is wider and it appears at about 300 °C. These peaks would be caused by the reduction of oxchloride compounds formed during the impregnation with H₂PtCl₆ and successive thermal treatments [52]. The shift to higher temperatures for the ZnAl₂O₄ COPR-supported catalysts could be due both to smaller particle sizes and the modification of the Pt-support interaction [14]. For both supports, the Sn(0.5)/ZnAl₂O₄ catalyst profile shows a small but very wide reduction zone from 200 to 250 °C to higher temperatures. In bimetallic PtSn/ZnAl₂O₄ catalysts, the main reduction peak of Pt is placed at 280–300 °C for the ZnAl₂O₄ MS support and at about 300 °C for the ZnAl₂O₄ COPR one. These shifts in the reduction temperature with respect to Pt monometallic catalysts together with certain widening of the peak could be attributed to a co-reduction of both metals that would form Pt-Sn alloys. Another wide and small peak at about 500–550 °C was observed, and it could correspond to the reduction of SnO₂ species. In PtSn/ZnAl₂O₄ COPR catalysts the same TPR peaks are observed, but shifted to higher temperature. The peak at 550 °C could be also due to the reduction of small quantities of free SnO₂ species stabilized in the support.

Fig. 5a and b shows TPR profiles of PtGe supported on ZnAl₂O₄ MS and ZnAl₂O₄ COPR. The Ge(0.5)/ZnAl₂O₄ catalysts supported on both ZnAl₂O₄ show a wide and poorly defined reduction zone that
Table 2
Activation energies of CHD and initial reaction rates in CHD and CPH ($R_{0\text{CH}}$, $R_{0\text{CP}}$) for Pt, PtSn and PtGe supported on ZnAl$_2$O$_4$ MS.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Activation energy (kcal/mol)</th>
<th>$R_{0\text{CH}}$ (mol/h g catal.)</th>
<th>$R_{0\text{CP}}$ (mol/h.g catal.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(0.3 wt.%)/ZnAl$_2$O$_4$ MS</td>
<td>17</td>
<td>32</td>
<td>0.70</td>
</tr>
<tr>
<td>PtSn(0.3 wt.%)/ZnAl$_2$O$_4$ MS</td>
<td>29</td>
<td>1</td>
<td>n.d.</td>
</tr>
<tr>
<td>PtSn(0.5 wt.%)/ZnAl$_2$O$_4$ MS</td>
<td>25</td>
<td>3</td>
<td>n.d.</td>
</tr>
<tr>
<td>PtGe(0.18 wt.%)/ZnAl$_2$O$_4$ MS</td>
<td>20</td>
<td>5</td>
<td>n.d.</td>
</tr>
<tr>
<td>PtGe(0.3 wt.%)/ZnAl$_2$O$_4$ MS</td>
<td>22</td>
<td>5</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

Table 3
Activation energies of CHD and initial reaction rates in CHD and CPH ($R_{0\text{CH}}$ and $R_{0\text{CP}}$) for Pt, PtSn and PtGe supported on ZnAl$_2$O$_4$ COPR.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Activation Energy (kcal/mol)</th>
<th>$R_{0\text{CH}}$ (mol/h.g catal.)</th>
<th>$R_{0\text{CP}}$ (mol/h.g catal.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(0.3 wt.%)/ZnAl$_2$O$_4$ COPR</td>
<td>14</td>
<td>72</td>
<td>0.70</td>
</tr>
<tr>
<td>PtSn(0.3 wt.%)/ZnAl$_2$O$_4$ COPR</td>
<td>22</td>
<td>10</td>
<td>n.d.</td>
</tr>
<tr>
<td>PtSn(0.5 wt.%)/ZnAl$_2$O$_4$ COPR</td>
<td>24</td>
<td>6</td>
<td>n.d.</td>
</tr>
<tr>
<td>PtGe(0.18 wt.%)/ZnAl$_2$O$_4$ COPR</td>
<td>25</td>
<td>4</td>
<td>n.d.</td>
</tr>
<tr>
<td>PtGe(0.3 wt.%)/ZnAl$_2$O$_4$ COPR</td>
<td>27</td>
<td>2</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

Fig. 4. TPR profiles of (PtSn (0.3 and 0.5 wt.%) catalysts supported on ZnAl$_2$O$_4$ MS (a) and ZnAl$_2$O$_4$ COPR (b). TPR of monometallic ones were added as a reference.

Fig. 5. TPR profiles of (PtGe (0.18 and 0.3 wt.%) catalysts supported on ZnAl$_2$O$_4$ MS (a) and ZnAl$_2$O$_4$ COPR (b). TPR of monometallic ones were added as a reference.
begins at about 200 °C and it is extended up to 700 °C, which could be attributed to the reduction of Ge4+ [53] for both supports. In the case of PtGe catalysts supported on ZnAl2O4 COPR and ZnAl2O4 MS (Fig. 5) two important reduction zones are observed, the first one with maxima at 220–280 °C and 300 °C, respectively, and the second one has a maximum at about 550 °C for both samples. The main Pt reduction peak in the monometallic catalyst gets wider with Ge addition because of the co-reduction of Pt and Ge with probable alloy formation or a catalytic effect of metallic Pt on the second metal reduction in either case. The second peak could be caused by the reduction of GeOx species in the vicinity of the metallic Pt.

Table 4 shows chemisorption values for different samples. The hydrogen chemisorption of the Pt/ZnAl2O4 COPR was higher than Pt/ZnAl2O4 MS. In general it was observed a decrease of the hydrogen chemisorption in the bimetallic catalysts. These results agree with several authors [54–56] that studied Pt and PtSn catalysts supported on Al2O3 and the results could be explained by synergy among three important factors: (i) electronic interactions between Pt and Sn with a probable alloy formation, which cannot chemisorb hydrogen, (ii) Sn surface enrichment which partially covers the Pt surface and (iii) blocking/dilution effect of Pt by Sn.

In the case of catalysts supported on ZnAl2O4 COPR, the second metal addition decreases the hydrogen chemisorptions. The second metal addition could not only form Pt-Sn or Pt-Ge alloys but also cover Pt crystallites with Sn or Ge, thus decreasing the H2 chemisorption capacity.

Moreover, TEM images of PtSn(0.5)/ZnAl2O4 MS and PtSn(0.5)/ZnAl2O4 COPR catalysts are shown in Fig. 6. For the PtGe catalysts that showed a low performance no further studies were done. Fig. 7 shows the particle size distribution (from TEM experiments) of PtSn(0.5)/ZnAl2O4 MS and PtSn(0.5)/ZnAl2O4 COPR catalysts. The particle size distributions (from TEM experiments) of PtSn/ZnAl2O4 MS catalyst were the following: 1–1.5 nm (34%), 1.5–2 nm (40%) and 2–2.5 nm (26%). The TEM characterization of the PtSn(0.5)/ZnAl2O4 COPR catalyst showed a particle size distribution of: 1–1.5 nm (57%), 1.5–2 nm (40%) and 2–2.5 nm (3.5%). In comparing the particle sizes of bimetallic catalysts with those of the monometallic ones, no noticeable differences were found which would indicate that the chemisorption decrease would not be caused by a particle size effect but electronic and/or geometric effects.

In order to determine the binding energies of Sn3d for PtSn(0.5)/ZnAl2O4 MS and PtSn(0.5)/ZnAl2O4 COPR catalysts, and Ge3d for PtGe(0.3)/ZnAl2O4 COPR catalyst, XPS measurements were done. In both bimetallic catalysts, Pt4f signal had binding energies between 314.1 and 313.6 eV that belongs to metallic Pt. Table 5 shows the binding energies and Sn/Pt and Ge/Pt surface atomic ratios from XPS analysis. It was not possible to discriminate between Sn3d5/2 binding energies of Sn(II) and Sn(IV) (486–487 eV) since their values are very close [57]. XPS spectra (Sn3d5/2 signal) of PtSn(0.5)/ZnAl2O4 MS and PtSn(0.5)/ZnAl2O4 COPR catalysts showed two peaks. Sn would be in two oxidation states: as oxidized Sn species (one portion in contact with Pt, and the other one in contact with the support) and in a lower proportion in zerovalent state, perhaps alloyed with Pt. It was found 26% of metallic Sn for PtSn(0.5)/ZnAl2O4 MS catalyst and 33% for PtSn(0.5)/ZnAl2O4 COPR catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Total V(H2 (mL H2 STP/g catal.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(0.3 wt.%)/ZnAl2O4</td>
<td>1.98 3.13</td>
</tr>
<tr>
<td>PtSn(0.5 wt.%)/ZnAl2O4</td>
<td>0.450 0.750</td>
</tr>
<tr>
<td>PtGe(0.3 wt.%)/ZnAl2O4</td>
<td>0.265 0.445</td>
</tr>
</tbody>
</table>
COPR catalyst. From Table 5 it can be observed an important surface enrichment of Sn since the Sn/Pt surface atomic ratio is higher, this being 35 for PtSn(0.5)/ZnAl2O4 MS catalyst and 36.5 for PtSn(0.5 wt.%)/ZnAl2O4 COPR one.

From XPS, TPR analysis and test reactions it can be concluded that the surface of reduced PtSn catalysts would be formed by metallic platinum, Sn(II) and/or Sn(IV) in high concentrations (some of them in contact with Pt) and smaller quantities of metallic Sn probably in alloyed phases with metallic Pt. No noticeable differences were found between the behaviour of both supports.

The XPS spectrum (Ge 3d signal) was made for PtGe(0.5)/ZnAl2O4 COPR catalyst. Ge 3d signals have a doublet at 3d3/2 and 3d5/2. It was not possible to determine the difference between Ge(II) and Ge(IV) species since there is a slight difference in their binding energies [58]. Ge 3d signal of PtGe(0.3)/ZnAl2O4 COPR catalyst showed three peaks. A high proportion of Ge is in an oxidized state (Ge(II) 64% and Ge(IV) 21%), probably in contact with Pt or with the support, and 15% of Ge would be as Ge(0), probably alloyed to Pt as TPR and test reactions confirm. From Table 5 it can be observed that there is a surface Ge enrichment, since the Ge/Pt surface atomic ratio is 28.

Results of hydrogen chemisorption and cyclohexane dehydrogenation rate would be related to geometric effects of dilution and/or blocking of Pt by Sn and also the formation of alloys or intermetallic Pt–Sn compounds as it was observed from the test reactions rather than a particle size effect as confirmed by TEM. Sn also exists as ionic species stabilized on the support. In the case of PtGe/ZnAl2O4 catalysts there are both electronic and geometrical (blocking and/or dilution) effects according to activation energy values, $k_e^{\text{Pt}} / k_e^{\text{PtGe}}$ and hydrogen chemisorption results. These effects reduced the concentration of exposed Pt. The defined reduction signals in TPR for PtGe/ZnAl2O4 catalyst showed that a fraction of Ge would be segregated and another part would be co-reduced with Pt and forming alloys. There would also be electronic effects as CHD reactions indicate. Besides, the alloyed particles exhibit low dehydrogenation and hydrogenolysis activities.

### 3.3. Catalytic tests

Fig. 8 shows the initial and final n-decane conversion for bimetallic PtSn and PtGe catalysts supported on ZnAl2O4 MS and ZnAl2O4 COPR. The behaviour of monometallic Pt/ZnAl2O4 MS and Pt/ZnAl2O4 COPR are also included for comparison. It can be observed that Pt/ZnAl2O4 COPR and Pt/ZnAl2O4 MS showed a similar average activity, the initial activity of Pt/ZnAl2O4 COPR catalyst was slightly higher than that of Pt/ZnAl2O4 MS. The bimetallic PtSn and PtGe catalysts show a higher activity than the corresponding monometallic Pt ones. It would be expected that the monometallic catalysts were more active than the bimetallic ones at the beginning of the reaction. However, if the carbon deposition in the first step of the reaction is higher in the monometallic catalysts than in bimetallic ones, the initial activity would decrease more rapidly in monometallic than in bimetallic samples. This coke deposition during the first 10 min of reaction time would produce a higher deactivation in Pt monometallic samples. It can be also observed that the initial activity (n-decane conversion) slightly increases as the Sn content increases for both supports, similar behavior with respect to Ge content is obtained with the PtGe catalysts. Besides, PtSn catalysts were more active than the PtGe ones. Furthermore, the bimetallic catalysts supported on ZnAl2O4 COPR were more active than those supported on ZnAl2O4 MS.

The results of catalyst deactivation measured by the DP values (defined as $DP = 100 \times (X_f - X^0)/X^0$, where $X^0$ and $X^f$ are the initial and the final n-decane conversions measured at 10 min and 130 min of the reaction time respectively) are shown in Fig. 9. It can be observed that the Pt/ZnAl2O4 MS catalyst (DP = 40.6%) has a lower decrease of activity than Pt/ZnAl2O4 COPR one (DP = 56.6%). This is in agreement with the total C deposited determined by TPO (0.75%C for Pt/ZnAl2O4 COPR and 0.27%C for Pt/ZnAl2O4 MS). These results indicate that the coke formation is an important factor in the catalyst deactivation. It must be indicated that Pt/ZnAl2O4 COPR had higher H2 chemisorption capacity, higher metallic dispersion and lower particle size than Pt/ZnAl2O4 MS. This means that Pt/ZnAl2O4 COPR has an important concentration of Pt sites which are active for dehydrogenation of large paraffins.

In the case of bimetallic catalysts, they had a lower deactivation than the corresponding monometallic ones (except for PtGe (0.3)/ZnAl2O4 MS). Besides, it can be observed that bimetallic catalysts supported on ZnAl2O4 COPR had a higher deactivation than the ones supported on ZnAl2O4 MS. Moreover, PtSn(0.5)/ZnAl2O4

### Table 5

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Binding energies Sn3d5/2 (eV)</th>
<th>Binding energies Ge3d3/2 (eV)</th>
<th>Atomic surface ratio Sn/Pt or Ge/Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtSn(0.5 wt.%)/ZnAl2O4 COPR</td>
<td>486.5 (74.1%)</td>
<td>485.8 (66.6%)</td>
<td>35</td>
</tr>
<tr>
<td>PtSn(0.5 wt.%)/ZnAl2O4 MS</td>
<td>484.6 (25.9%)</td>
<td>485.8 (66.6%)</td>
<td>36.5</td>
</tr>
<tr>
<td>PtSn(0.18 wt.%)/ZnAl2O4 COPR</td>
<td>484.5 (33.4%)</td>
<td>30.6 (64%)</td>
<td>28</td>
</tr>
<tr>
<td>PtSn(0.18 wt.%)/ZnAl2O4 MS</td>
<td>32.4 (21%)</td>
<td>29.1 (15%)</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 8. Initial n-decane conversion ($X^0$) and final n-decane conversion ($X^f$) for PtSn (0.3 and 0.5 wt.%) and PtGe (0.18 and 0.3 wt.%) supported on ZnAl2O4 MS (a) and ZnAl2O4 COPR (b). X$: at 10 min of the reaction time and X*: at 130 min of the reaction time.
between these parameters probably due to the low carbon content. MS catalyst has the lowest DP, while PtGe(0.3)/ZnAl2O4 MS sample displays the highest deactivation of all bimetallic catalysts. It could be concluded that all PtGe catalysts showed a higher deactivation than the corresponding PtSn for both supports. This difference is more marked for the bimetallic catalysts supported on ZnAl2O4 MS. For example, the DP for PtSn(0.5)/ZnAl2O4 COPR is 38.7% while for PtSn(0.5)/ZnAl2O4 MS is 19.4%. The addition of a second metal (Sn or Ge) increased the activation energy in CHD, thus indicating an electronic modification probable due to alloys formation. This effect was slightly more pronounced for PtSn catalysts than for PtGe ones when the support MS is used. Minor differences were found in bimetallic catalysts supported on ZnAl2O4 COPR.

Fig. 10 shows the relationship between DP, previously defined, and the carbon content determined by TPO (at the end of the reaction) for different catalysts. It can be concluded that there is a good correlation between DP and the final coke content for the catalysts supported on ZnAl2O4 COPR. In the case of catalysts supported on ZnAl2O4 MS it was not possible to obtain a good correlation between these parameters probably due to the low carbon content.

As it was previously mentioned, undesirable side reactions and coke deposition can be important factors that influence the catalytic performance. For example, the DP for PtSn(0.5)/ZnAl2O4 COPR is 38.7% while for PtSn(0.5)/ZnAl2O4 MS is 19.4%. The addition of a second metal (Sn or Ge) increased the activation energy in CHD, thus indicating an electronic modification probable due to alloys formation. This effect was slightly more pronounced for PtSn catalysts than for PtGe ones when the support MS is used. Minor differences were found in bimetallic catalysts supported on ZnAl2O4 COPR.

The addition of the second metal decreases the amount of deposited carbon with respect to that of the monometallic ones. Besides, the Sn or Ge addition to Pt favours the n-decane dehydrogenation to olefins, minimizing other undesirable reactions, since the electronic and geometric effects (which appear to be slightly higher for Sn than for Ge) are present. These effects can decrease the interaction strength of the olefins with the metallic sites, thus maintaining the metallic surface with low amount of the coke. This effect appears to be more pronounced when the second metal content increases. de Miguel et al. [61] found a similar effect for PtSn and PtGe catalysts supported on Al2O3 and MgO. Besides, TPO experiments of the PtSn(0.5)/ZnAl2O4 MS and PtSn(0.5)/ZnAl2O4 COPR were made at 10 min of the beginning of the reaction too, and the results showed that the coke deposition was practically negligible (<0.1 wt.%), thus showing that the bimetallic PtSn catalysts had low initial deactivation in contrast to the monometallic ones.

Fig. 11 shows the TPO profiles of Pt supported on ZnAl2O4 MS and ZnAl2O4 COPR at the end of the n-decane dehydrogenation reaction. It can be observed that the support has an important effect on the amount of deposited carbon. In fact, it is clearly noted that the Pt/ZnAl2O4 MS catalyst has lower carbon deposition than the Pt/ZnAl2O4 COPR one. Besides, the TPO of used Pt/ZnAl2O4 MS shows a burning peak at low temperature, which indicates that an important carbon fraction is deposited on the metal. On the other hand, the Pt/ZnAl2O4 COPR catalyst shows that carbon is mainly deposited on the support.

Fig. 12 displays TPO profiles taken at the end of n-decane dehydrogenation reaction for PtSn (0.5) (a) and PtGe (0.3) (b) catalysts supported both on ZnAl2O4 MS and ZnAl2O4 COPR. It can be observed not only the effect of the support but also the effect of the second metal addition. In the case of PtSn(0.5)/ZnAl2O4 COPR it is observed a broad peak between 310 and 550 °C, which corresponds to carbon deposited on the metallic function (although in minor proportion) and on the support (in a major quantity) [62–65]. In the case of the PtSn(0.5)/ZnAl2O4 MS catalyst, it was observed a low amount of carbon deposited on the metallic phase although with low toxicity according to the results above mentioned. From TPO profile of PtSn(0.3)/ZnAl2O4 COPR catalyst, it can be observed a peak with a maximum at 470 °C which can be attributed to the burning of an important amount of coke mainly deposited on the support [63–66]. In the case of the TPO profile of PtGe(0.3)/ZnAl2O4 MS, it can be observed a broad peak which begins at low temperature. This result would indicate that the important amount of coke deposited on the support is due to the interaction of the coke with the support.
carbon deposited on the metallic phase and has a different toxicity. In fact, the coke deposited on this catalyst is clearly lower than that deposited on the catalyst supported on ZnAl2O4 COPR, but their DP is higher than the second one, which means a higher toxicity of the carbon deposited on PtGe(0.3)/ZnAl2O4 MS catalyst.

Fig. 13 displays the results of average selectivities (along the reaction time) to \(<\text{C}_{10}\), \([\text{C}_{10}]\) and to \([\text{i-c C}_{10}]\) in the n-decane dehydrogenation for mono and bimetallic catalysts supported on ZnAl2O4 MS y ZnAl2O4 COPR. It must be noted that it is possible to determine average selectivities since the selectivity to each group of products slightly changes with the reaction time.

**Fig. 11.** TPO profiles of Pt supported on ZnAl2O4 MS and ZnAl2O4 COPR at the end of the n-decane dehydrogenation reaction.

**Fig. 12.** TPO profiles of PtSn (a) and PtGe (b) catalysts supported on ZnAl2O4 MS and ZnAl2O4 COPR after the n-decane dehydrogenation reaction.

**Fig. 13.** Average selectivity to \(<\text{C}_{10}\> (a), [\text{C}_{10}]> (b), [\text{i-c C}_{10}> (c) and 1-decene (d) in n-decane dehydrogenation for mono and bimetallic catalysts supported on ZnAl2O4 MS and ZnAl2O4 COPR.
Fig. 13a shows the average selectivities (in the reaction time) to \(<C_{10}\) in the n-decane dehydrogenation for mono and bimetallic catalysts supported on ZnAl₂O₄ MS and ZnAl₂O₄ COPR. The light paraffins are produced by breaking of C-C bonds, and they can be produced by two ways: (i) cracking via acid sites (cracking of olefins produced by dehydrogenation in the metallic phase) and (ii) hydrogenolysis catalyzed by metallic centers \([40,60,61]\). Olefins are cracked or isomerized more quickly than linear paraffins. Taking into account the neutral characteristic of the supports, the reactions catalyzed by acid centres have a low participation. It must be noted that the selectivity to \(<C_{10}\) is practically the same for both Pt monometallic catalysts, which is in agreement with the hydrogenolytic capacity of these catalysts. It should be remembered that the low acidity of both supports does not appear to play an important role in the reaction. It is also observed that Sn or Ge addition to monometallic catalysts produces a decrease of the selectivity to \(<C_{10}\), this effect being more pronounced for catalysts supported on ZnAl₂O₄ MS. Besides, PtSn catalysts are less selective to \(<C_{10}\) than PtGe ones, mainly those supported on ZnAl₂O₄ MS. The lower selectivities to \(<C_{10}\) of the bimetallic catalyst supported on ZnAl₂O₄ MS respect to the one supported on ZnAl₂O₄ COPR are due to the higher acidity of the last one. Furthermore, the second metal addition produces a poisoning effect on the acidity \([3,60,66]\), which leads to bimetallic catalysts with low degradation capacity of the raw paraffin.

The average selectivities to other monoolefins (except α-monoolefin), diolefins, dienes, trienes, etc., \(\{C_{10}\}\) are shown in Fig. 13b. It must be indicated that these reactions are very fast and they are produced on the metallic phase. This Figure shows that Pt and bimetallic catalysts supported on ZnAl₂O₄ MS have higher selectivities to \(\{C_{10}\}\) than the same catalysts supported on ZnAl₂O₄ COPR. Besides, the Sn or Ge addition to Pt/ZnAl₂O₄ MS or Pt/ZnAl₂O₄ COPR does not produce an important modification of the selectivity to \(\{C_{10}\}\). Furthermore, it is also observed that the Sn or Ge loading have slight influence on the selectivity to \(\{C_{10}\}\), and PtGe catalysts were slightly more selective than the PtSn ones, for both supports.

The average selectivities to non-linear chains (including branched chains, isoparaffins, iso-olefins, cyclization products, aromatics, alkyl aromatics) \(\{i-c\ C_{10}\}\) are shown in Fig. 13c. The aromatization reaction (dehydrocyclization of paraffins) is a fast and structure-sensitive one \([40]\) and it can be produced through a bifunctional mechanism, where the olefins produced on the metal can migrate to the acidic function for a further cyclization. The mechanism of consecutive dehydrogenation, first on the metallic sites and then on the acidic ones can be represented by the following scheme:

\[
\begin{align*}
\text{n-decane} & \rightarrow \text{dehydrogenation} \\
& \rightarrow \text{cyclization}
\end{align*}
\]

In this group of products \(\{i-c\ C_{10}\}\) the isomerization products from the original paraffins are included. The isomerization (fast reaction) can be produced on the acidic sites of the supports and in a lower quantity on the metallic sites. It must be noted that the average selectivity to \(\{i-c\ C_{10}\}\) for the Pt/ZnAl₂O₄ MS catalyst is slightly lower than for Pt/ZnAl₂O₄ COPR one, and it is favoured by the higher acidity of the support. The average selectivities to \(\{i-c\ C_{10}\}\) for bimetallic catalysts are higher than those of the corresponding monometallic ones, independently of the support. These surprising results would be not expected, and the explanation of these phenomena is that the average selectivities were calculated after 10 min of the reaction beginning. It must be considered that during the first 10 min of the reaction there is an important deposition of coke (both on the metal phase and the support) in the monometallic samples with respect to the bimetallic ones, which would inhibit in an important way the olefin formation, leading to isomerization and cyclization reactions in the monometallic catalysts and decreasing the selectivity to \(\{i-c\ C_{10}\}\). The bimetallic catalysts show opposite effects where the cyclization is less affected than dehydrogenation by the second metal addition. In general, mono and bimetallic catalysts supported on ZnAl₂O₄ COPR were more selective to \(\{i-c\ C_{10}\}\) than those supported on ZnAl₂O₄ MS.

As regards the average selectivity to 1-decene of the catalysts supported on both ZnAl₂O₄ are shown in Fig. 13d. It could be observed that the bimetallic catalysts were more selective to 1-decene than the corresponding monometallic ones supported on ZnAl₂O₄ MS and show lower deactivation. The bimetallic catalysts supported on ZnAl₂O₄ COPR showed a higher selectivity to 1-decene than monometallic ones.

In analyzing the selectivity to 1-decene of the catalysts with the reaction time, the fall of the initial selectivities in the monometallic catalysts were higher than for the corresponding bimetallic ones, independently of the support. According to Fig. 6 the conversion level for the monometallic catalysts is lower than the bimetallic ones even for the initial conversion. This behaviour can be related to an important carbon deposition on monometallic catalysts in contrast with the lower carbon deposition in the bimetallic systems as it was mentioned. With the Sn or Ge addition to Pt, the selectivity to 1-decene mainly in the catalysts supported on ZnAl₂O₄ MS is increased. Sn and Ge produce electronic-geometric modifications of the metallic phase leading to a decrease of the hydrogenolytic capacity, thus increasing the selectivity to 1-decene. Besides, the lower acidity of ZnAl₂O₄ MS favours the dehydrogenation since it decreases the side undesirable reactions, like hydrocracking and polymerization. Moreover, the addition of a second metal (Sn or Ge) to Pt would lead to a weak interaction olefins-metallic phase \([3,51,62]\), which inhibits the consecutive dehydrogenation of the monoolefin. This could be attributed to the modification of Pt ensembles by Sn or Ge (geometric and electronic effects), which decreases the olefins adsorption strength, thus avoiding the subsequent transformation into dienes.

Fig. 14 shows initial and final yields to 1-decene (\(Y\), \(Y = \text{conversion} \times \text{selectivity} \rightarrow 1\)-decene; \(Y_0\): initial, at 10 min of reaction time and \(Y_f\): final, at 130 min of the reaction beginning)
4. Conclusions

It was possible to obtain ZnAl₂O₄ by mechanochemical synthesis (MS) or coprecipitation (COPR) with good surface area and low acidity to minimize subsequent reactions of the monoolefins formed during the n-decane dehydrogenation and low coke formation rate since these support surfaces lead to metal structures probably scattered on edges and corners. From the metallic characterization, PtSn/ZnAl₂O₄ catalysts showed geometric effects of dilution and/or blocking of Pt by Sn and also the formation of alloys or intermetallic Pt–Sn compounds. In the case of PtGe/ZnAl₂O₄ catalysts there were both electronic and geometrical (blocking and/or dilution) reducing the concentration of exposed Pt. A Ge fraction would be segregated and another part would be co-reduced with Pt and forming alloys. Bimetallic catalysts were more active than the monometallic ones with lower deactivation. PtSn catalysts on both supports, the yield to 1-decene is higher for PtSn catalysts than for PtGe ones. With reference to the effect of the second metal loading on the yield to 1-decene, it is observed a positive one when the loading increases.

PtSn(0.5)/ZnAl₂O₄ MS catalyst has a yield to 1-decene slightly lower than that of PtSn(0.5)/ZnAl₂O₄ COPR one, although the first catalyst is more stable with the reaction time and it has a lower deactivation. These characteristics determine a good catalytic formulation. The higher initial and final yields to 1-decene of PtSn/ZnAl₂O₄ COPR catalyst could be due to the more efficient first catalyst is more stable with the reaction time and it has a lower deactivation. These characteristics determine a good catalytic formulation rate since these support surfaces lead to metal structures probably scattered on edges and corners. From the metallic characterization, PtSn/ZnAl₂O₄ catalysts showed geometric effects of dilution and/or blocking of Pt by Sn and also the formation of alloys or intermetallic Pt–Sn compounds. In the case of PtGe/ZnAl₂O₄ catalysts there were both electronic and geometrical (blocking and/or dilution) reducing the concentration of exposed Pt. A Ge fraction would be segregated and another part would be co-reduced with Pt and forming alloys. Bimetallic catalysts were more active than the monometallic ones with lower deactivation. PtSn catalysts on both supports, the yield to 1-decene is higher for PtSn catalysts than for PtGe ones. With reference to the effect of the second metal loading on the yield to 1-decene, it is observed a positive one when the loading increases.

PtSn(0.5)/ZnAl₂O₄ MS catalyst has a yield to 1-decene slightly lower than that of PtSn(0.5)/ZnAl₂O₄ COPR one, although the first catalyst is more stable with the reaction time and it has a lower deactivation. These characteristics determine a good catalytic formulation. The higher initial and final yields to 1-decene of PtSn/ZnAl₂O₄ COPR catalyst could be due to the more efficient first catalyst is more stable with the reaction time and it has a lower deactivation. These characteristics determine a good catalytic formulation.