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Alkyne Selective Hydrogenation with Mono- and Bimetallic-Anchored Catalysts

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Abstract

Partial hydrogenation of alkynes has industrial and academic relevance on a large scale; industries such as petrochemical, pharmacological and agrochemical use these compounds as raw material. Finding an economic, active and selective catalyst for the production of alkenes through partial hydrogenation of alkynes is thus an important challenge. Mono- and bimetallic catalysts (palladium, ruthenium and nickel) were synthesized by the incipient wetness technique using gamma alumina and an activated carbon as supports. The catalysts were characterized by inductively coupled plasma, hydrogen chemisorption, temperature-programmed reduction and X-ray photoelectron spectroscopy (XPS). The objective of this work is to study 1-heptyne-selective hydrogenation using supported catalysts influenced by different factors: (a) pretreatment reduction temperature, (b) reaction temperature, (c) type of support, (d) metal loading, (e) precursor salt and (f) addition of a second metal to monometallic palladium catalyst. The Lindlar commercial catalyst, commonly used in these types of reactions, was used for comparative purposes. XPS technique allowed verifying that the presence of electron-deficient species on the catalyst surface with high metal loading affects the conversion and selectivity to the desired product. Nevertheless, the influence of geometrical effects and/or mixed active sites in the catalysts, as well as metal-metal and metal-support interactions, cannot be neglected.

Keywords: selective hydrogenation, alkyne, alkene, heterogeneous catalysts, mono- and bimetallic catalysts

1. Introduction

Petroleum cuts contain mixtures of unsaturated and aromatic compounds. Among them, acetylenic hydrocarbons are very unstable; so they must be transformed to olefins. Alkenes have industrial and academic relevance on a large scale; industries such as petrochemical, pharmaceutical and agrochemical use these compounds as raw materials. Partial hydrogenation reactions using catalytic materials allow a reduction in operational costs and also enable high selectivity to alkenes. Specifically, the catalytic selective hydrogenation of alkynes using either homogeneous or heterogeneous catalysts has been widely studied in the past several years [1]. The hydrogenation of any alkyne conduces naturally to the alkene formation as the former trends to bind more strongly than the latter on the supported metal catalyst, thus blocking the possibility of the alkene readsorption or displacing it from the support surface. Many natural products, such as biologically active compounds [2], are synthesized through this kind of reactions.

Classical heterogeneous catalysts used to hydrogenate multiple carbon-carbon bonds contain noble metals such as Pd, Pt, Ru and Rh, which are highly active and selective [3, 4]. Many authors have found that supported palladium catalysts present the highest catalytic activity for the partial hydrogenation of alkynes to alkenes [5, 6]. One of the most used catalytic systems for these kinds of reactions is the Lindlar catalyst (Pd/CaCO₃ modified with Pb(OAc)₂), developed in 1953 [7]. During decades, much research has been carried out modifying this type of catalyst in order to increase the activity and selectivity to alkenes of low molar weight. Several materials have been used as supports, and they are usually classified as organic (macroreticular/macroporous polymers) or inorganic (silica, alumina, zeolites and clays). Besides, modified palladium [8] or nanoparticles of Pd have also been investigated [9]. Another kind of material, not clearly included in any of these groups, is carbonaceous species, whose outstanding properties as a catalyst support are well recognized [10], among them are the possibility of modifying the specific surface area, the porosity and the surface chemistry; moreover, carbon supports present the advantage of being inert in liquid reaction media [11]. Many catalysts, mono- or bimetallic as well as complexes of several transition metals, have also been proposed for these kinds of reactions [2, 12–14]. A major part of research efforts have been devoted to the partial hydrogenation of short-chain alkynes such as ethyne [15], with few works related to longer chain alkynes. As Pd has increased its cost, it is a challenge to synthesize cheaper catalysts. In this context, using nickel catalysts during the selective hydrogenation of alkyne is less studied and has been recently researched [12].

Based on the above considerations, the objectives of this chapter are to evaluate the effects of different factors on the activity and selectivity during the selective hydrogenation of 1-heptyne, a long-chain terminal alkyne. The factors studied are (a) pretreatment reduction temperature, (b) reaction temperature, (c) type of support, (d) metal loading, (e) precursor salt and (f) addition of a second metal (such as nickel) to monometallic palladium catalyst. Last but not least, all the catalytic performances are compared against those obtained with the commercial Lindlar catalyst.

2. Experimental details

2.1. Catalysts preparation

All the monometallic catalysts used in this work were prepared by the incipient wetness technique, and for bimetallic catalyst the successive impregnation technique was used following a procedure previously indicated [12]. γ - Al_2O_3 (Ketjen CK 300, cylinders of 1.5 mm diameter) and a pelletized activated carbon (AC: GF-45 provided by NORIT) were used as supports.

All of the supports were impregnated with acid aqueous solutions of PdCl_2 or $\text{Pd}(\text{NO}_3)_2$ (Fluka, purity of >99.98%), and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Fluka, purity of >98.5%) was used as the precursor salt for the bimetallic catalyst.

The monometallic alumina-based catalysts were calcined at 823 K for 3 h. Before its catalytic evaluation, all the catalysts were reduced for 1 h under a hydrogen stream at 573 K. Only the High loaded Pd catalyst prepared with chlorine precursor salt was reduced at 373 and 573 K to study the effect of pretreatment temperature on the catalytic behaviour. Besides, the bimetallic catalyst was reduced for 1 h at 673 K.

2.2. Catalysts characterization

Physical adsorption of gases (N_2 at 77 K and CO_2 at 273 K) and mercury porosimetry were used to determine the pore volume distribution and the specific surface area for both supports and the specific surface area [16]. Both adsorptives (N_2 and CO_2) allow estimating the pore volume distribution for pores with a diameter up to 7.5 nm approximately. From Dubinin-Radushkevich equation to the CO_2 isotherm at 273 K, it is possible to obtain the micropore volume (V_{micro}), while the supermicropore volume (V_{sm}) is attained by the subtraction of V_{micro} to the volume calculated by the same equation but applied to the N_2 adsorption isotherm at 77 K. By mercury porosimetry using a Carlo Erba 2000 equipment, macropore volume (V_{macro}) and part of the mesopore volume (V_{meso}) were determined. The rest of V_{meso} was obtained from N_2 adsorption isotherm and Hg porosimetry as described previously [17].

Using ICP Perkin Elmer equipment, metal loadings of the catalysts were measured.

Micromeritics AutoChem II 2920 was used to determine the H_2 chemisorption of Pd at 303 K using 0.2 g of catalyst. *In situ* sample reduction was performed using a H_2/Ar stream (5% v/v), ensuring the absence of beta-phase palladium hydride on the catalyst surface. The samples were degassed *in situ* for 2 h in an argon flow (AGA purity of 99.99%) and cooled up to 303 K. Then, the hydrogen uptake was measured by sending calibrated pulses. The metal dispersion was calculated assuming a $\text{H}:\text{Pd} = 1$ stoichiometry [18].

Temperature programmed reduction, TPR, of the samples was performed using a Micromeritics AutoChem II 2920. Gamma-alumina-supported catalysts were pretreated for 30 min at 673 K under an O_2 stream, and cooled with an Ar stream (AGA purity of 99.99%). The palladium anchored on GF-45 was pretreated with an argon flow at the same operational

conditions used for alumina-based catalysts. The TPR profiles were obtained increasing the temperature up to 1223 K at 10 K min⁻¹ in a 5% (v/v) hydrogen/argon stream.

Electronic states of Pd, Cl or N were measured using a VG Microtech Multilab equipment following a procedure elsewhere published [19]. The reference-binding energies (BEs) were Al 2p at 74.4 eV and C 1s peak at 284.5 eV for alumina and carbonaceous catalysts, respectively.

2.3. Catalytic evaluations

The performed reaction test was the selective hydrogenation of 1-heptyne. **Figure 1** shows the scheme of 1-heptyne hydrogenation reaction; the possible products obtained are 1-heptene (desired product) and n-heptane.

A stainless steel reactor was used during the catalytic evaluations. Catalyst of 0.75 g, a hydrogen pressure of 150 kPa and temperatures of 298 and 303 K were used. Seventy-five millilitres of 5% (v/v) 1-heptyne (Fluka, purity of >98%) in toluene (Merck, purity of >99%) solution was used as feed. The possibility of diffusional limitations during the catalytic tests was assessed following a procedure previously described [20]. Experiments were carried out at different stirring velocities in the 180–1400 rpm range. Stirring velocities higher than 500 rpm allowed obtaining identical values of activity and selectivity for all of the catalysts. On the other hand, the catalyst particle size was varied verifying that the conversion and selectivity were the same (within experimental error) than those for the non-crushed catalysts. Therefore, chemical control ensures neither external nor internal diffusional limitations during the catalytic tests.

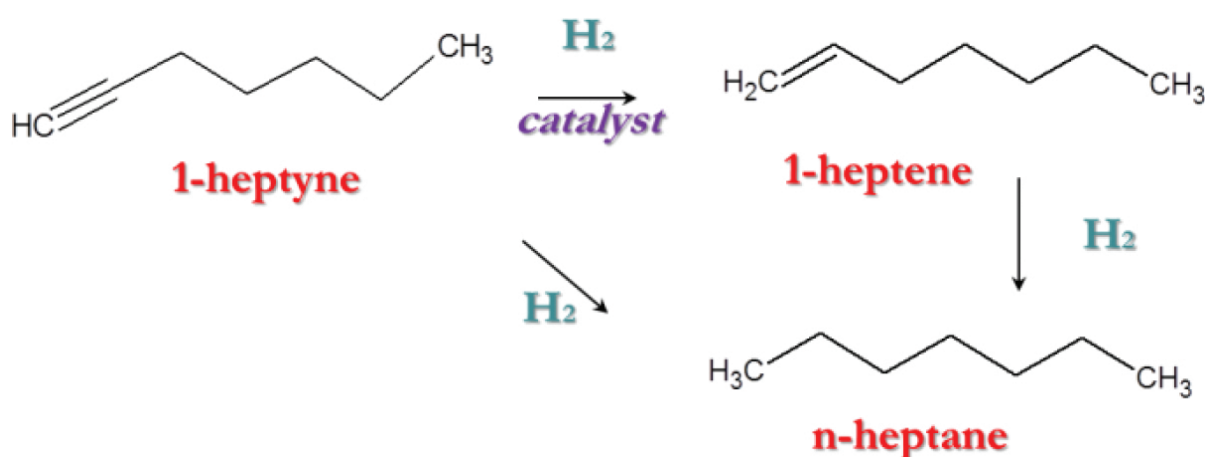


Figure 1. Scheme for the 1-heptyne hydrogenation.

Gas chromatography (GC) using a flame ionization detector (FID) with a capillary column (Chrompack CP WAX 52 CB) was used to analyse 1-heptyne, 1-heptene and n-heptane.

3. Results and discussion

3.1. Catalysts characterization

Table 1 presents the Brunauer-Emmett-Teller (BET) surface area and micro-, supermicro-, meso- and macropore volumes (S_{BET} , V_{micro} , V_{sm} , V_{meso} and V_{macro} respectively) of the $\gamma\text{-Al}_2\text{O}_3$ and AC supports. It can be observed that the activated carbon (AC) includes almost the same amounts of the four types of pores, with a large proportion of pore volume in the range of supermicro-, micro-, meso- and macropores, the so-called transport pores while $\gamma\text{-Al}_2\text{O}_3$ is a mesoporous solid having a poor contribution of supermicro-, micro- and macropores.

| Support | S_{BET} ($\text{m}^2 \text{g}^{-1}$) | V_{micro} (mL g^{-1}) | V_{sm} (mL g^{-1}) | V_{meso} (mL g^{-1}) | V_{macro} (mL g^{-1}) |
|-------------------------|---|---|--|--|---|
| Al_2O_3 | 180 | 0.048 | 0.030 | 0.487 | 0.094 |
| AC | 1718 | 0.345 | 0.498 | 0.449 | 0.400 |

Table 1. BET surface area and pore volume distribution of the supports [16].

Table 2 contains the catalyst notation used according to the precursor salt, metal loading or reduction temperature used during the catalysts preparation. Besides for all of the studied catalysts, dispersions (D), XPS results and activity values (turnover frequency (TOF)) calculated considering a kinetic of zero order are reported in **Table 2**.

| Catalysts | Precursor salt | Metal loading (wt%) | Reduction Temp (K) | D (%) | XPS | | TOF (s^{-1}) |
|---------------------------------------|-----------------------------------|---------------------|--------------------|-------|------------------------------|-----------------------|-------------------------|
| | | | | | Pd 3d _{5/2} BE (eV) | Cl/Pd or N/Pd (at/at) | |
| Pd _(5%) /Al ₃₇₃ | PdCl ₂ | 4.69 Pd | 373 | 42 | 337.0 | 0.6 | 9.1×10^{-3} |
| Pd _(5%) /Al | PdCl ₂ | 4.69 Pd | 573 | 28 | 336.5 | 0.2 | 1.8×10^{-2} |
| Pd _(5%) /AC | PdCl ₂ | 4.82 Pd | 573 | 32 | 336.8 | 0.3 | 4.9×10^{-3} |
| Pd _(0.4%) /Al | PdCl ₂ | 0.44 Pd | 573 | 58 | 334.9 | – | 5.1×10^{-2} |
| PdN _(0.4%) /Al | Pd(NO ₃) ₂ | 0.37 Pd | 573 | 32 | 334.9 | – | 1.1×10^{-1} |
| Pd-Ni/Al | Pd(NO ₃) ₂ | 0.37 Pd | 673 | 31 | 334.2 ^(54%) | – | 1.6×10^{-1} |
| | Ni(NO ₃) ₂ | 0.89 Ni | | | 335.3 ^(46%) | | |

Table 2. Catalysts naming convention, precursor salt, metal loading, reduction temperature, dispersion values, XPS BE of Pd 3d_{5/2}, Cl/Pd or N/Pd atomic ratios and TOF values for all of the catalysts.

As it can be seen in **Table 2**, the dispersion values for Pd_(5%)/Al catalyst decrease as the reduction temperature increases owing to the agglomeration of Pd particles. Also, at the same reduction temperature (573 K), palladium supported on AC presents slightly higher dispersion than

when alumina is used as support possibly because of the high surface area of AC [21] or to the different porosity of the supports. Besides, a decrease in the metal loading, using the same precursor salt, produces a significant increase in the dispersion value as the palladium active sites are most exposed on the catalyst surface. On the other hand, at the same reduction temperature, the change of precursor salt produces a higher dispersion when PdCl_2 is used because of complex oxychlorinated species formation during the calcination process. These species, $\text{Pd}^{\delta+}\text{O}_x\text{Cl}_y$, present a stronger interaction with the support than that showed by PdO , thus improving the metal dispersion [22].

Additionally, as nickel monometallic catalysts do not consume hydrogen during the chemisorption analysis, the dispersion value of bimetallic Pd-Ni/Al catalyst was calculated taking into account only the Palladium active sites. It can be noted that the dispersions of $\text{PdN}_{(0.4\%)}\text{/Al}$ and Pd-Ni/Al catalysts are very similar, confirming that nickel in the bimetallic catalyst does not chemisorb H_2 during the analysis. Last but not least, the dispersion values in **Table 2** are in total accordance with those reported by other authors [23].

In **Table 2**, Pd $3d_{5/2}$ BE and the Cl/Pd or N/Pd superficial atomic ratios obtained by XPS technique are also listed. Low-loaded monometallic catalysts, $\text{Pd}_{(0.4\%)}\text{/Al}$ and $\text{PdN}_{(0.4\%)}\text{/Al}$, present the Pd $3d_{5/2}$ peak with a binding energy equal to 334.9 eV that corresponds to Pd^0 [24], whereas high-loaded monometallic catalysts, $\text{Pd}_{(5\%)}\text{/Al}_{373}$, $\text{Pd}_{(5\%)}\text{/Al}$ and $\text{Pd}_{(5\%)}\text{/AC}$, displayed peak values of BE at 337.0, 336.5 and 336.8 eV, respectively. These higher binding energy values indicate that the metal is electron-deficient ($\text{Pd}^{\delta+}$) possibly because of the presence of non-reduced Pd oxychloride species formed during the calcination process [22] or to non-reduced Pd species stabilized by neighbouring Cl atoms [23, 25]. The XPS BE results indicate that the reduction temperature influences the electronic state of palladium in $\text{Pd}_{(5\%)}\text{/Al}$ catalysts: the one reduced at 373K has a peak at 337.0 eV, whereas that reduced at 573 K presents a peak shifted to 336.5 eV. Therefore, the low reduction temperature used generates a more electron-deficient Pd (337.0 eV) with a high Cl superficial content. On the other hand, high-loaded monometallic catalysts present Pd with a slightly higher electron deficiency ($\text{Pd}^{\delta+}$ species) and a higher concentration of superficial Cl when Pd is anchored on GF-45.

In the case of the Pd-Ni/Al bimetallic catalyst after the deconvolution of the Pd $3d_{5/2}$ BE, two signals can be seen at 334.2 eV (54% of all of the metal species, atomic basis) and 335.3 eV (46 at/at%) palladium species. These values suggest the presence of two type of Pd species in simultaneous, represented by $\text{Pd}^{\delta-}$ (electron-rich species) and slightly electron-deficient palladium species ($\text{Pd}^{\delta+}$, with δ close to 0), respectively. The former could be attributed to the formation of metallic bonds or alloy, occurring at low temperatures [26, 27]. Additionally, for Pd-Ni/Al catalyst, the BE of Ni $2p_{3/2}$ peak appears at 856.4 eV, which is attributed to electron-deficient species (Ni^{n+} , with n close to 2) probably corresponding to different interactions between nickel and aluminium (from the support) [28], or to the formation of intermediate Pd-Ni- Al_2O_3 surface species [12].

The XPS spectra of high-loaded monometallic catalysts prepared from chlorine precursors show a peak at ca. 198.5 eV that corresponds to Cl $2p_{3/2}$. The peak was associated to surface chloride species [24] that were not completely eliminated after reduction. Besides, neither Cl nor N was detected by XPS on the surface for the low-loaded monometallic catalysts.

The TPR profiles of palladium mono- and bimetallic catalysts are shown in **Figure 2**. In this figure, it can be seen that all the prepared catalysts present a main reduction peak at low temperatures, between 259 and 358 K, that can be attributed to the reduction of palladium oxidized species (PdO_x) to Pd^0 [29]. Besides, the low-loaded catalysts present the reduction peak shifted to lower temperatures, indicating that Pd species are more easily reduced than those present on high-loaded catalysts. These shifts to higher temperatures are due to different types of the metal-support interactions.

For the low-loaded catalysts, $\text{Pd}_{(0.4\%)}/\text{Al}$, $\text{PdN}_{(0.4\%)}/\text{Al}$ and $\text{Pd-Ni}/\text{Al}$, the profiles in **Figure 2** show an inverted peak between 335 and 339 K, which could be assigned to the decomposition of the β -PdH phase that is formed during the reduction of the PdO_x particles at low temperatures [22, 29, 30].

The TPR profiles for the high-loaded catalysts prepared from PdCl_2 salt ($\text{Pd}_{(5\%)}/\text{Al}$ and $\text{Pd}_{(5\%)}/\text{AC}$) show a second broad peak between 400 and 600 K, which is attributed to the reduction of $\text{Pd}^{\delta+}\text{O}_x\text{Cl}_y$ species [19, 22].

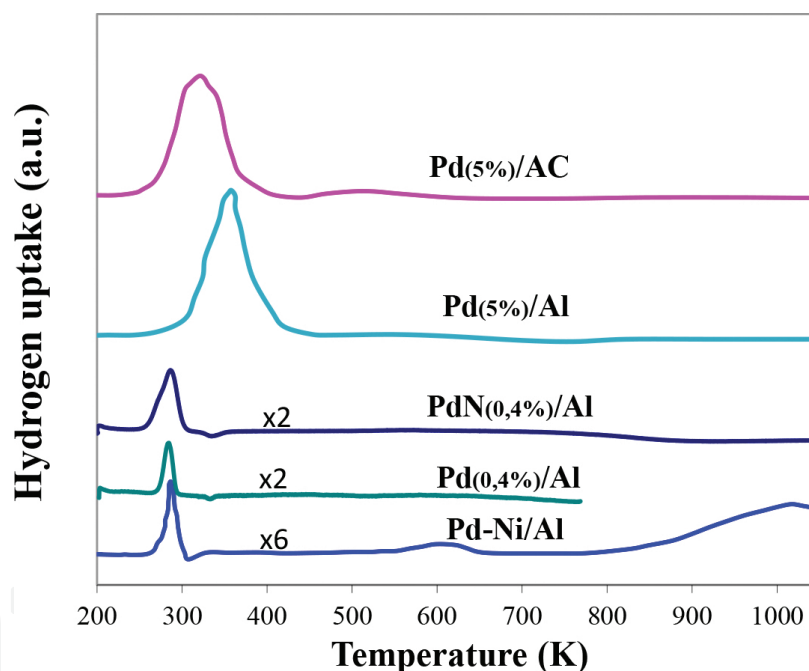


Figure 2. TPR profiles for $\text{Pd}_{(5\%)}/\text{Al}$, $\text{Pd}_{(5\%)}/\text{AC}$, $\text{Pd}_{(0.4\%)}/\text{Al}$, $\text{PdN}_{(0.4\%)}/\text{Al}$ and $\text{Pd-Ni}/\text{Al}$.

The TPR profile of the bimetallic catalyst $\text{Pd-Ni}/\text{Al}$ is also presented in **Figure 2**. Up to 500 K, the reduction profile is very similar to the monometallic $\text{PdN}_{(0.4\%)}/\text{Al}$ catalyst, having its main reduction peak at 286 K corresponding to PdO_x reduction. The decomposition of the β -PdH phase is also present at lower temperature, 307 K; the shift of this signal suggests that the decomposition of the β -PdH phase is more easily accomplished in the bimetallic catalyst. Furthermore, as shown in **Figure 2**, the bimetallic catalyst has a second peak at 621 K, which is attributed to the reduction of NiO species to Ni^0 [31–33]. It is well known that nickel monometallic catalysts prepared from nitrate salts are reduced at temperatures between 600

and 1000 K when the contact between NiO and alumina is intimate [33–35]. The patterns of reduction depend on the nature of the metal-support interactions, which can be modified by the calcination temperature employed during the preparation of the monometallic nickel catalysts [34]. Besides, a broad peak is also present in this profile with a maximum at 1000 K, which is attributed to the reduction of nickel aluminates, NiAl_2O_4 , showing a strong metal-support interaction [35, 36]. According to the calculated degree of reduction, determined by TPR, the bimetallic catalyst has a low percentage of reduced Ni (7%) and Pd (74%). This suggests the presence of strong Pd-Ni intermetallic interaction in the catalyst; however, the interaction of Pd and Ni with the support cannot be neglected.

When palladium-supported catalysts are used during the alkyne hydrogenations, the β -phase hydride acts as a hydrogen source that promote over hydrogenation to obtain mainly the alkane, decreasing the selectivity to the alkene. The disappearance of the β -PdH phase is very important because it could impact directly on the activity and selectivity [37]. These authors state that the disappearance of the β -PdH phase considerably decreases alkynes hydrogenation rate to alkanes, thus increasing the selectivity to alkenes formation. For the prepared mono- and bimetallic catalysts, the palladium β -phase Pd hydride is not present as it is proved by the TPR profiles at the pretreatment reduction temperature adopted.

According to XPS and TPR characterizations, it can be concluded that after pretreatment Pd^0 is present in the low-loaded monometallic catalysts, while $\text{Pd}^{\delta+}\text{O}_x\text{Cl}_y$ species are formed in the high-loaded Pd catalysts. On the other hand, on the bimetallic catalyst, two kinds of palladium species ($\text{Pd}^{\delta+}$, with δ close to 0, and $\text{Pd}^{\delta-}$) and Ni^{n+} (with n close to 2) are present on the surface.

3.2. Catalytic evaluations

3.2.1. Effect of the reduction temperature

Figure 3 presents 1-heptyne total conversion and selectivity to 1-heptene as a function of time for $\text{Pd}_{(5\%)}/\text{Al}$ catalyst pretreated for 1 h in a hydrogen flow at 373 and 573 K, the reaction temperature was 303 K. In the figure, it can be seen that the total conversion increases as the reduction temperature is increased, while the selectivity is slightly lower at the higher reduction temperature ($\geq 90\%$). From the TOF values displayed in **Table 2**, it may be concluded that the catalyst reduced at higher temperature is nearly twice more active than when it is reduced at 373 K. The activity results can be explained taking into account the electronic state of Pd in each catalyst: the more electron-deficient palladium species the less active is the catalyst for the hydrogenation of 1-heptyne. It is probably that the $\text{Pd}^{\delta+}$ species inhibit the interaction between the metal and 1-heptyne due to an electronic effect, decreasing its electron-donor character. Therefore, it can say that the presence of electron-deficient $\text{Pd}^{\delta+}\text{O}_x\text{Cl}_y$ species improves the selectivity to the desired product. Given that the chlorine is not completely removed from the $\text{Pd}_{(5\%)}/\text{Al}$ catalyst after the heat treatments, it seems likely that the role of the remaining chlorine on the catalyst surface could be to stabilize the positively charged palladium structures, resulting in less active but more selective catalysts (electronic and steric factors). Therefore, our results suggest a correlation between the reduction temperature, electron deficiency of palladium species and chloride content, with total conversion and

selectivity. In total accordance with our results, an increase in selectivity was found by some authors [38] when smaller and more electron-deficient Pd clusters were used. Other authors [39] found that 1-heptene is more weakly adsorbed than 1-heptyne on electron-deficient Pd species and, once formed, the 1-heptene molecules are more easily desorbed than 1-heptyne. This effect was previously found for other partial hydrogenation reactions using monometallic Ru-supported catalysts [40].

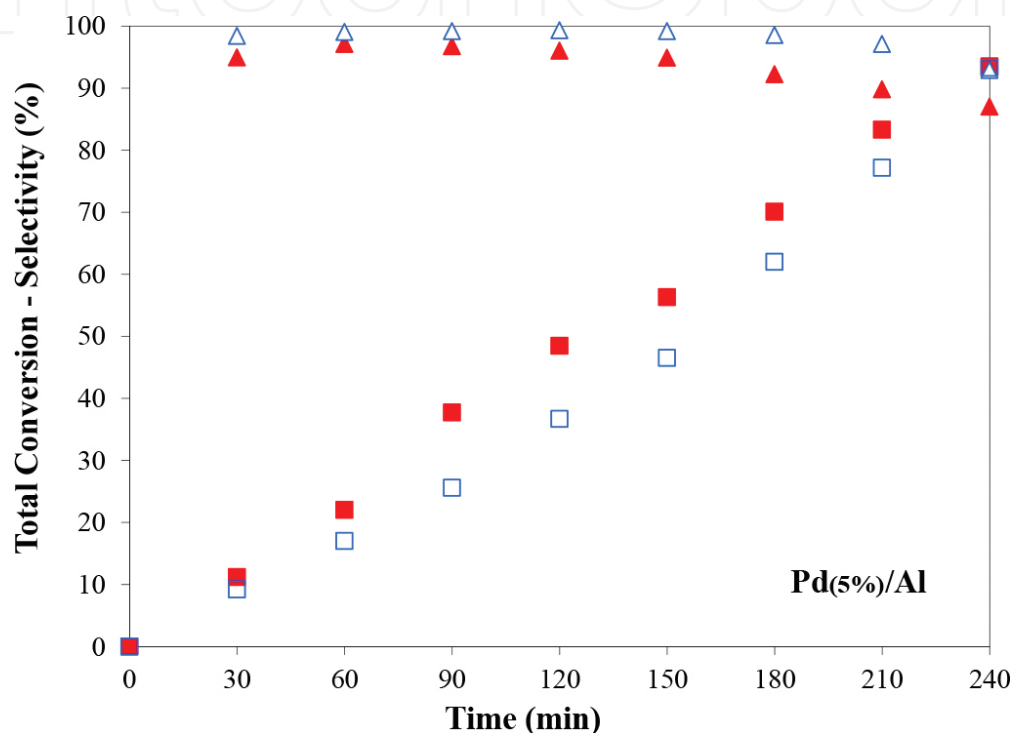


Figure 3. Effect of reduction temperature: Total conversion of 1-heptyne (■, □) and selectivity to 1-heptene (▲, △) as a function of time for Pd_(5%)/Al catalyst: reduced at 573 K (filled symbols) and reduced at 373 K (opened symbols). Reaction temperature: 303 K.

According to the obtained results, 573 K was selected as the reduction temperature of the monometallic catalysts because higher values of total conversions were obtained.

3.2.2. Effect of reaction temperature

Another important factor to evaluate is the reaction temperature. Alkyne hydrogenation reactions must be carefully controlled, especially at large scale when large amount of catalyst are used as in these kinds of exothermic reactions. It is well known that above 313 K, a complete hydrogenation of the alkyne compounds occurs [5]. In order to evaluate this effect, the reaction tests were performed at 280 and 303 K using the Pd_(5%)/Al catalyst reduced for 1 h at 573 K (optimal reduction temperature). In **Figure 4**, the total conversion and selectivity to 1-heptene as a function of time at the mentioned temperatures are presented.

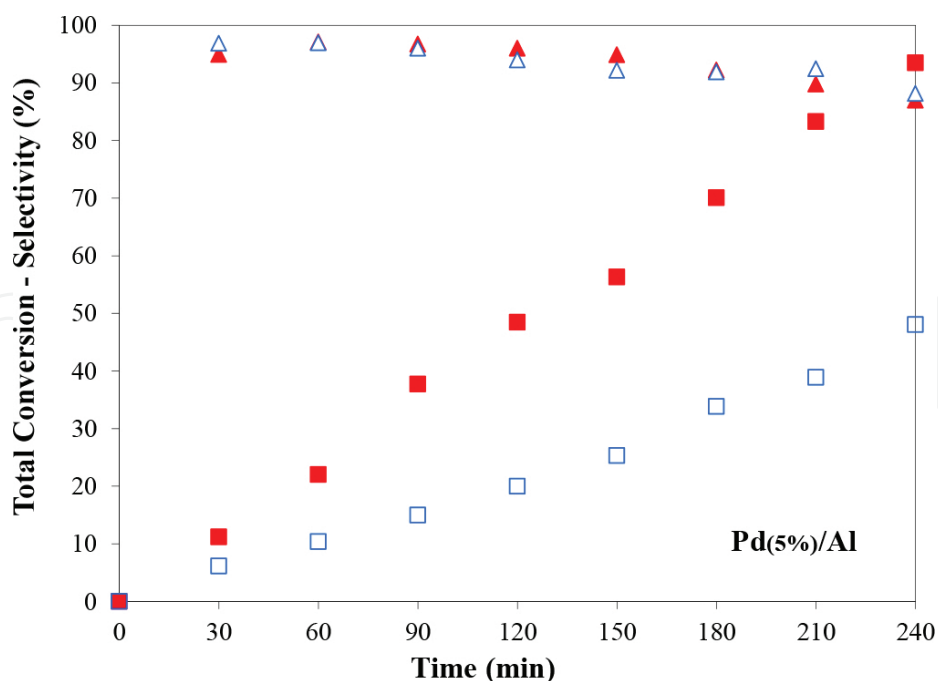


Figure 4. Effect of reaction temperature: Total conversion of 1-heptyne (■, □) and selectivity to 1-heptene (▲, △) as a function of time for Pd_(5%)/Al catalyst: 303 K (filled symbols) and 280 K (opened symbols). Reduction temperature: 573 K.

The obtained results shown in **Figure 4** indicate a marked difference in the total conversion of 1-heptyne when the reaction temperature is increased. The total conversion is markedly higher when the reaction is carried out at 303 K, while similar selectivity to 1-heptene values is obtained at both temperatures. Other authors have found similar results while studying the partial hydrogenation of several alkynes [41, 42].

As hydrogenation reactions are extremely exothermic, an increase in the reaction temperature does not favour the reaction thermodynamically, but it improves the kinetic of the reaction. Experimental results show that the optimum reaction temperature is 303 K because higher total conversions of 1-heptyne are obtained with high selectivity to 1-heptene ($\geq 90\%$).

3.2.3. Effect of support

It is important to compare different materials employed as supports of the active phases, so two kinds of supports were selected: alumina (inorganic) and activated carbon (a carbonaceous material, called AC). The evaluated catalysts were Pd_(5%)/Al and Pd_(5%)/AC, reduced for 1 h at 573 K and run at 303 K. The total conversion and selectivity to 1-heptene versus time are shown in **Figure 5**.

Analysing the data presented in **Figure 5** and the TOF values shown in **Table 2**, it can be noted that better performance is achieved when Al₂O₃ is used as support. Initially, the obtained selectivity values with both supports are higher than 90%, but for total conversion higher than 60% the selectivity to 1-heptene slightly decays.

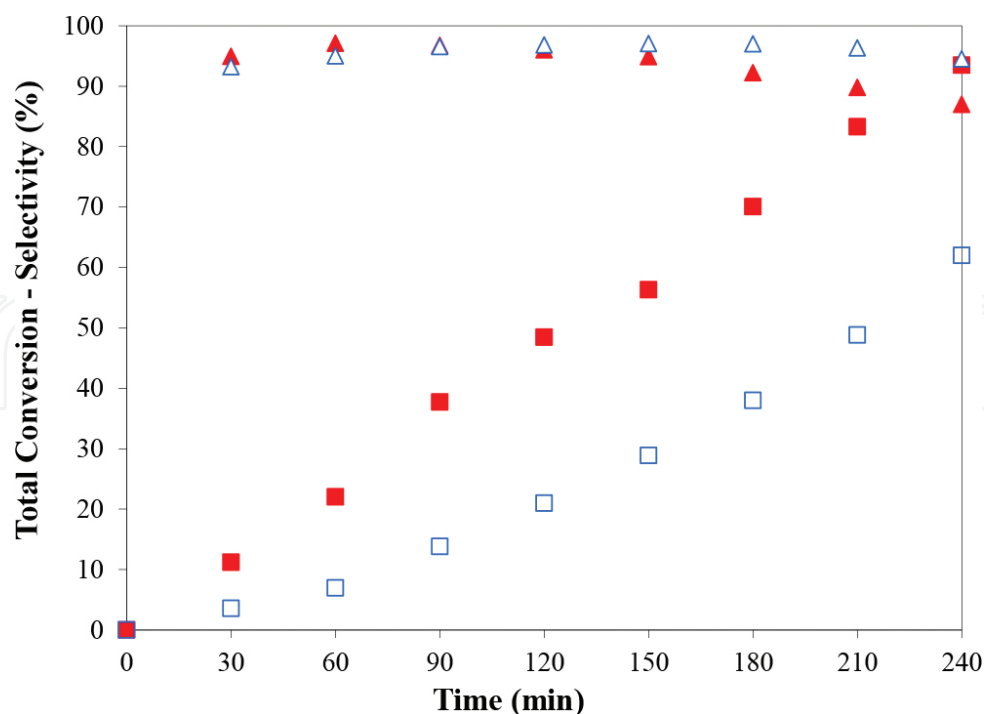


Figure 5. Effect of support: Total conversion of 1-heptyne (■, □) and selectivity to 1-heptene (▲, △) as a function of time for Pd_(5%)/Al (filled symbols) and Pd_(5%)/AC (opened symbols). Reduction and reaction temperatures: 573 and 303 K, respectively.

As both catalysts present quite similar dispersion values as well as Pd^{δ+} electron-deficient species and Cl/Pd atomic ratios, the observed differences in activity must be assigned to the characteristic of the support. The influence of the support on the physicochemical properties and, therefore, on the catalytic behaviour of metals is well established in the literature [43].

During the preparation step of the catalysts, the specific support properties of the carbons (such as chemical nature, texture, pore structure, surface state, etc.) can modify the morphology and/or localization of the metal particles, electronic structure of the surface metal atoms, adsorption-desorption equilibrium of reactants, and so on. This can generate differences in the conversion and selectivity values. Thus, as our results suggest, the activity and selectivity of palladium-supported catalysts is a complex property of the whole catalyst and cannot be related to a single parameter. Considering the above, the slightly higher selectivity to 1-heptene at the highest conversion values found for Pd_(5%)/AC catalyst could be associated to shape selectivity induced by the porous support. In this way, this might be due to the 1-heptene molecule has a planar end, unlike the more voluminous end of the fully saturated n-heptane. The increase of the selectivity to the desired product may be associated with the localization of the Pd species in narrow pores (micro- and supermicropores) in the carbon support. If this is the case, it could also be suggested that the lower total conversion of Pd_(5%)/AC catalyst is due to the narrower porosity of the activated carbon, as it is probable that fewer 1-heptyne molecules could reach the active sites located in the supermicropores. If a significant fraction of the active species are located in pores of a particular size (larger supermicropores, practically absent in Pd_(5%)/Al catalyst, and mesopores), the concentration of 1-heptene in the neighbour-

hood of the Pd species could be enhanced, thus favouring the consecutive hydrogenation of 1-heptene to heptane. Although the surface chemistry of GF-45 support is quite unlike that of alumina, the similar dispersions and electronic states of palladium on $\text{Pd}_{(5\%)}/\text{Al}$ and $\text{Pd}_{(5\%)}/\text{AC}$ reinforce the idea that their different catalytic behaviours are related to the differences in the support porosities.

3.2.4. Effect of the metal loading

The price of a metal, its toxicity, easy handling and safety are a set of properties to take into account during the preparation of the catalysts. Industrially profitable processes with highly active, selective and cheaper catalysts are continually researched. As the cost of the catalyst is important, a reduction of the metal loading on the final catalyst was considered and its effect on activity and selectivity during the hydrogenation reaction was assessed.

In **Figure 6**, the total conversion and selectivity to 1-heptene for the palladium catalysts supported on alumina with a metal loading of 5 and 0.4 wt% of Pd are presented. The used precursor salt was PdCl_2 , the catalysts were reduced at 573 K and the catalytic tests were carried out at 303 K.

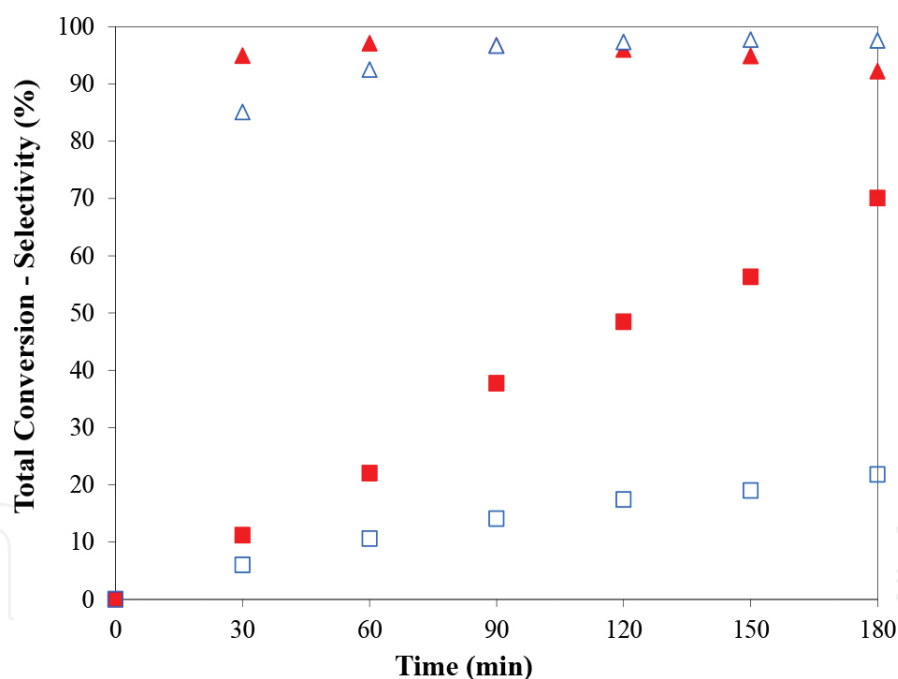


Figure 6. Effect of metal loading: Total 1-heptyne conversion (■, □) and selectivity to 1-heptene (▲, △) as a function of time for $\text{Pd}_{(5\%)}/\text{Al}$ (filled symbols) and $\text{Pd}_{(0.4\%)}/\text{Al}$ (opened symbols). Reduction and reaction temperatures: 573 and 303 K, respectively.

In the figure, it can be seen that decreasing the metal concentration of the catalyst, at identical operational conditions, decreases the total conversion (70–22% at 180 min). On the other hand, considering TOF values of both catalyst shown in **Table 2**, it can be concluded that the low-loaded $\text{Pd}_{(0.4\%)}/\text{Al}$ catalyst is 2.8 times more active than the $\text{Pd}_{(5\%)}/\text{Al}$. The selectivities to the

desired product (1-heptene) were 95% average without large changes when the metal loading is decreased. This fact is very important from an economic and industrial point of view.

It is well known that during hydrogenation reactions, metallic centres rich in electrons can cleave the bond in H_2 by means of the interaction of a filled d metal orbital with the empty sigma antibonding molecular orbital of H_2 [44]. The rupture of the hydrogen bond is more easily done on metals with a high amount of available electrons in the external d orbital, as it is the case of $Pd_{(0.4\%)} / Al$ (with Pd^0). This rupture should be less likely on metals with fewer d electrons, as in the case of $Pd_{(5\%)} / Al$ (with $Pd^{\delta+}$ species). Therefore, the differences in activity between the reported catalysts could be partly attributed to differences in the electronic density of the external d orbital of each metal (electronic factor). So, the high activity of $Pd_{(0.4\%)} / Al$ could be attributed to different factors: (a) palladium totally reduced Pd^0 , which favours the dissociative adsorption of hydrogen (electronic factor), (b) high dispersion of the low-loaded catalyst indicating that a high amount of small active sites are present on the surface (geometric factor) and (c) the absence of chlorine, a bulky and electronegativity element, which prevent the adsorption of the alkyne (steric factor).

3.2.5. Effect of precursor salt

The effect of precursor salt (palladium chloride and nitrate) on the total conversion and selectivity to 1-heptene during the 1-heptyne partial hydrogenation was studied using $Pd_{(0.4\%)} / Al$ and $PdN_{(0.4\%)} / Al$ catalysts reduced in a hydrogen flow at 573 K and tested at 303 K. The results of total conversion and selectivity to 1-heptene are shown in **Figure 7**.

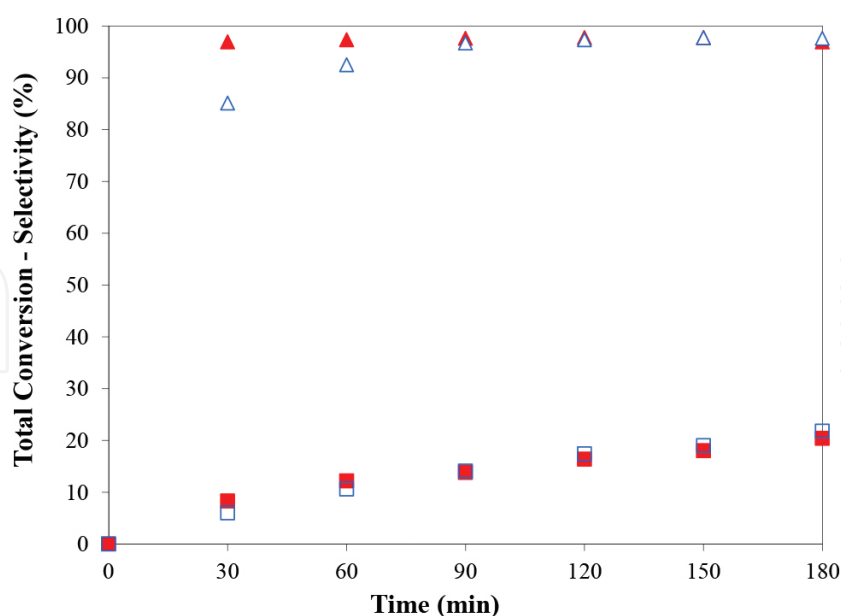


Figure 7. Effect of precursor salt. Total conversion of 1-heptyne (\blacksquare , \square) and selectivity to 1-heptene (\blacktriangle , \triangle) as a function of time for $PdN_{(0.4\%)} / Al$ (filled symbols) and $Pd_{(0.4\%)} / Al$ (opened symbols). Reduction and reaction temperatures: 573 and 303 K, respectively.

In **Figure 7**, it can be observed that both catalysts present very similar behaviour on 1-heptyne total conversions and on selectivity to 1-heptene. As shown in Section 3.1, the characterization techniques indicated the presence of reduced palladium after the pretreatment with hydrogen flow at 573 K, and also there is neither chlorine nor nitrogen species on the surface of both catalysts (absence of electronic and steric factor). As different dispersions were obtained with chemisorption analysis, differences in TOF (shown in **Table 2**) indicate that $\text{PdN}_{(0.4\%)}/\text{Al}$ is twice active than $\text{Pd}_{(0.4\%)}/\text{Al}$. So, geometric factors are responsible of the higher activity of $\text{PdN}_{(0.4\%)}/\text{Al}$.

3.2.6. Effect of the addition of a second metal: bimetallic catalyst

As the low-loaded palladium catalyst prepared with the nitrate precursor salt was more active than that prepared with chloride salt, the addition of Ni to the monometallic $\text{PdN}_{(0.4\%)}/\text{Al}$ catalyst was evaluated in order to improve 1-heptyne total conversion. In **Figure 8**, 1-heptyne total conversion and selectivity to 1-heptene as a function of time obtained during the hydrogenation test for the monometallic $\text{Pd}_{(0.4\%)}/\text{Al}$ and bimetallic Pd-Ni/Al catalysts are plotted. The bimetallic catalyst was reduced for 1 h at 673 K, and the temperature of the catalytic evaluations was 303 K.

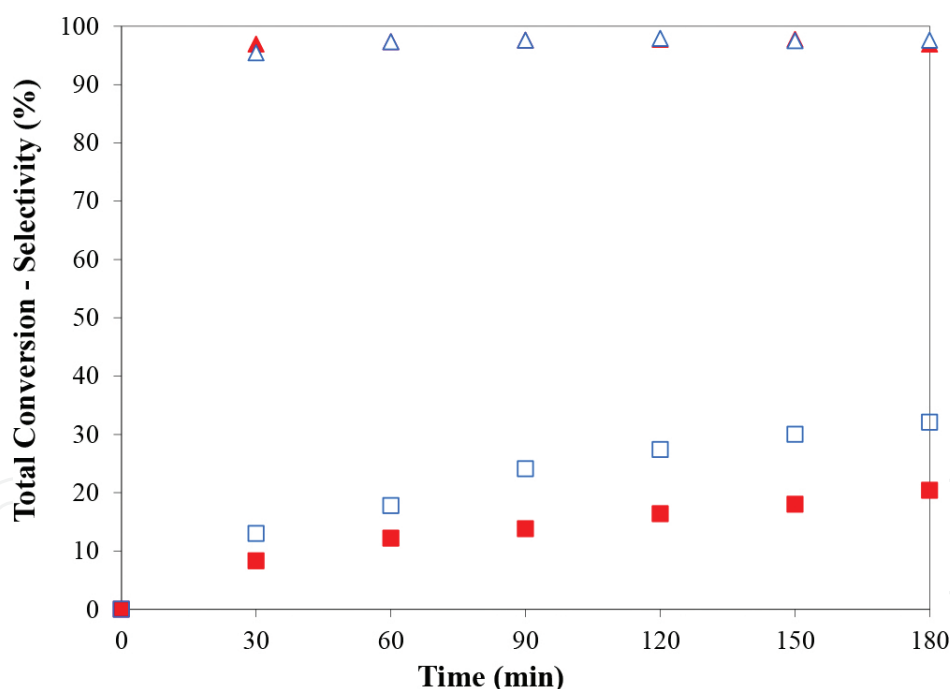


Figure 8. Effect of the addition of Ni: Total conversion of 1-heptyne (■, □) and selectivity to 1-heptene (▲, △) as a function of time for $\text{PdN}_{(0.4\%)}/\text{Al}$ (filled symbols) and Pd-Ni/Al (opened symbols). Reduction and reaction temperatures: 573 and 303 K, respectively.

According to **Figure 8**, the bimetallic and monometallic catalysts present similar and very high selectivities to the desired product (97% c.a.). Therefore, it can be said that the addition of Ni as a second metal to the alumina-supported palladium catalysts has no influence on the

selectivity to 1-heptene. Therefore, the disappearance of the beta-phase palladium hydride could be the cause, at least in part, of the high selectivities found for mono- and bimetallic palladium catalysts. Besides, the nickel addition to the palladium monometallic catalyst improves 1-heptyne total conversion. TOF values indicate that Pd-Ni/Al is 1.5 times more active than Pd_(0.4%)/Al. There is not a simple interpretation to explain the influence of the second metal on the Pd performance. Alkyne partial hydrogenation reactions are more or less sensitive to geometrical and electronic effects, the latter being the most important ones.

As observed by XPS, the nickel addition to the palladium catalyst promotes electron deficiency of Ni (Niⁿ⁺) and Pd (Pd^{δ+}), and generates electron-rich palladium species (Pd^{δ-}). Since the bimetallic catalyst has a high amount of available electrons in the *4d* Pd orbital than monometallic PdN_(0.4%)/Al, the hydrogen cleavage would be favoured on this catalyst. This would explain the higher activity of the bimetallic Pd-Ni catalyst. The modification of the electronic state of Pd could be responsible for the better catalytic behaviour, moreover considering the high electronic density of the triple bond. However, the influence of geometrical effects and/or mixed sites on the activity of the bimetallic catalyst cannot be discarded.

3.2.7. Commercial Lindlar catalyst

The Lindlar catalyst is very often used as a reference for the selective hydrogenation of alkynes, so in this work the performance of the commercial catalyst at 303 K was obtained. **Figure 9** presents the total conversion of 1-heptyne and selectivity to 1-heptene versus reaction time for this catalyst.

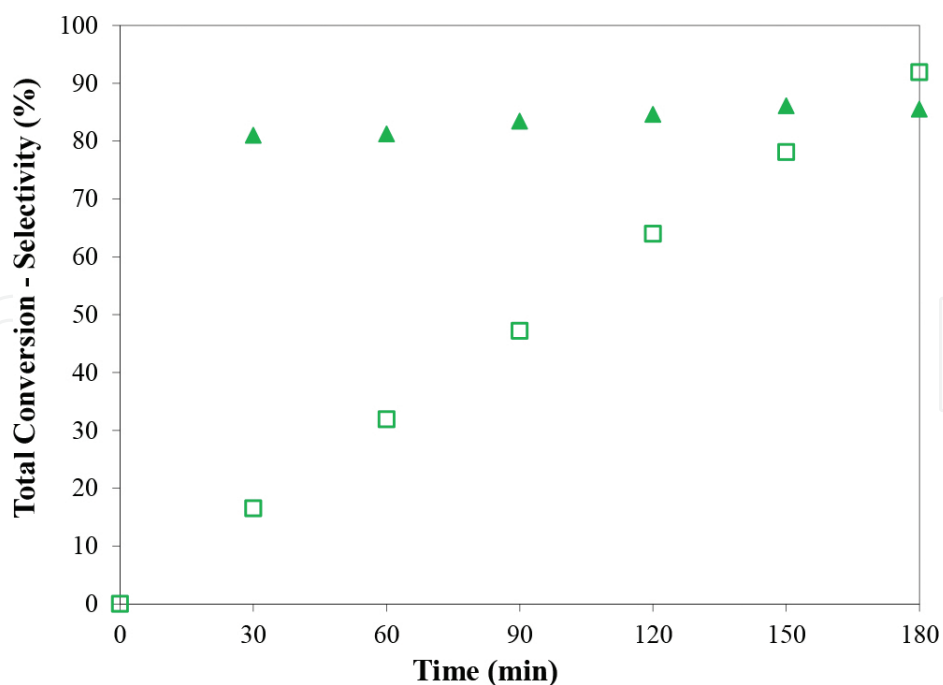


Figure 9. Commercial Lindlar catalyst: Total conversion to 1-heptyne (□) and selectivity to 1-heptene (▲) as a function of time for Lindlar catalyst. Reaction temperature: 303 K.

In **Figure 9**, it can be observed that the Lindlar catalyst allows obtaining high values of 1-heptyne total conversion with high selectivity to 1-heptene, between 82% and 86%. Comparing the results obtained with the prepared high-loaded catalysts (5 wt% of Pd, similar to that of Lindlar), a slightly better yield to 1-heptene is obtained with the Pd_(5%)/Al catalyst than that obtained with Lindlar catalyst. Besides, it must be remarked that the prepared catalyst has the advantage of being a pelletized material. On the other hand, the lowest yield to 1-heptene is obtained with Pd_(5%)/AC. Differences in total conversion can be associated to electronic effects, as the surface palladium species on the Lindlar catalyst are more electron-deficient than those present on Pd_(5%)/Al or Pd_(5%)/AC.

3.3. Final considerations

In **Figure 10**, the initial 1-heptyne hydrogenation rates (calculated per gram of palladium) and the selectivities to the desired product (1-heptene) at 180 min for all of the synthesized catalysts against Lindlar catalyst results are compared.

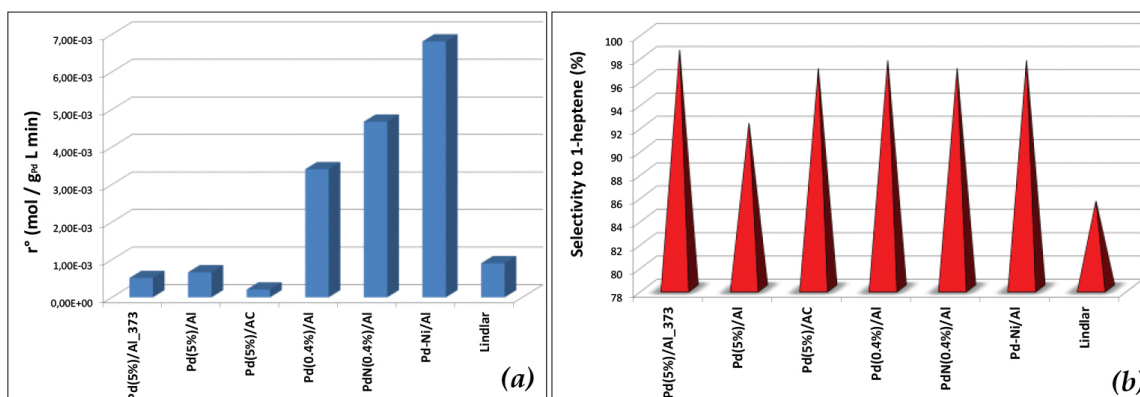
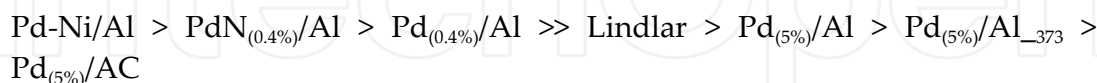
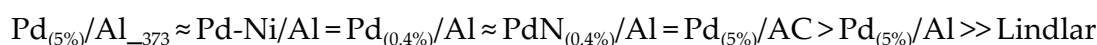


Figure 10. Comparison of initial 1-heptyne hydrogenation rates (a) and selectivities to 1-heptene at 180 min (b) for the catalytic systems evaluated in the present chapter.

According to the results obtained and shown in **Figure 10**, the tested catalysts showed the following order of activity:



With the following order of selectivities:



From **Figure 10**, it can be concluded that the prepared pelletized catalysts are more active and selective than the Lindlar catalyst.

Finally, pelletized catalysts have additional advantages against the Lindlar catalyst: the easy and cheap way of recovering the catalytic systems from the remaining solution at the end of the industrial process.

4. Conclusions

A series of palladium mono- and bimetallic catalysts were synthesized, characterized and tested during the partial hydrogenation of a terminal alkyne. All the prepared catalysts are active and highly selective for the partial hydrogenation of 1-heptyne under mild reaction conditions. Various factors were studied, and the behaviour of the catalysts on activity and selectivity during the hydrogenation of 1-heptyne was evaluated. The studied factors and the principal conclusions obtained are condensed below:

1. *Variation of reaction and reduction temperatures:* Pd_(5%)/Al catalyst was reduced at two temperatures (373 and 573 K) before its catalytic evaluation and was tested at 280 and 303 K. The optimum reaction temperature to obtain high activity with high yield of 1-heptene (desired product) is 303 K. On the other hand, high activity values are accessed when the reduction temperature is 573 K.
2. *Different support:* Alumina and activated carbon were used as supports of the palladium catalysts. The results show that higher activities are obtained when alumina is used as support. The differences in the support porosities could be the cause of the differences between Pd_(5%)/Al and Pd_(5%)/AC catalytic behaviour. Nevertheless, more experimental work is necessary to reach a better understanding about the effect of the support on the catalytic behaviour of the catalysts studied.
3. *Metal loading:* The decrease of the metal loading leads to cheaper catalysts, particles more dispersed on the catalyst surface, metal species easier to reduce, with better activities, maintaining high selectivity values.
4. *Precursor salt:* In this particular case of 1-heptyne partial hydrogenation, between nitrate and chlorine precursors, a better activity is obtained with PdN_(0.4%)/Al. It can be remarked that this catalyst is the most active system. However, it should be noted that the chlorine species are necessary in order to increase the selectivity (steric and electronic factors due to chloride species).
5. *Bimetallic catalyst:* The addition of a second metal, as nickel to palladium monometallic catalyst, modifies the electronic state of palladium leaving it with electron-deficient and electron-rich species, even though the influence of geometrical effects and/or mixed sites cannot be neglected. Nickel proved to be a good promoter for the palladium monometallic catalyst as it caused an increment in the activity without modifying the high selectivity to 1-heptene characteristic of Pd monometallic catalysts. Besides, this bimetallic catalyst presents the advantages of low Pd loading and low cost of the nickel salt, which leads to a cheaper and highly active and selective catalyst.
6. *Comparison with commercial Lindlar catalyst:* All catalysts synthesized during the present study show better selectivity values to the desired product (1-heptene) than Lindlar catalyst. This makes them valuable catalytic materials for the alkyne hydrogenation reactions and as an alternative option to the expensive commercial catalyst. In addition, Lindlar presents the disadvantage of being a non-pelletized material and must be operated

under slurry conditions; therefore, the reagent solution must be purified after the reaction through an uneconomic method to recover the catalyst.

Finally, considering XPS results, this chapter allows concluding that the presence of electron-deficient species on the catalyst surface of the catalysts with high metal loading is an important factor and influences on the activity and selectivity to the desired product. Nevertheless, the influence of geometrical effects and/or mixed sites in the catalysts as well as metal-metal and metal-support interactions cannot be neglected.

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References

- [1] L'Argentièrre PC, Cagnola EA, Liprandi DA, Román- Martínez MC, Salinas-Martínez de Lecea C. Carbon-supported Pd complex as catalyst for cyclohexene hydrogenation. *Appl. Catal. A: Gen.* 1998; 172: 41–48.
- [2] Ulan JG, Wilhelm FM. Mechanism of 2-hexyne hydrogenation on heterogeneous palladium. *J. Mol. Catal.* 1989; 54 (2): 243–261.
- [3] Teschner D, Vass E, Hävecker M, Zafeiratos S, Schnörch P, Sauer H, Knop-Gericke A, Schlögl R, Chamam M, Wootsch A, Canning AS, Gamman JJ, Jackson D, McGregor J, Gladden LF. Alkyne hydrogenation over Pd catalysts: A new paradigm. *J. Mol. Catal.* 2006; 242: 26–37. DOI:10.1016/j.jcat.2006.05.030.

- [4] Kačer P, Kuzma M, Červený L. The molecular structure effects in hydrogenation of cycloalkylsubstituted alkynes and alkenes on Pt and Pd catalysts. *App. Catal. A: Gen.* 2004; 259: 179–183. DOI:10.1016/j.apcata.2003.09.025.
- [5] Nishimura S. *Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis*. Canada: John Wiley & Sons, Inc.; 2001, pp. 148–169. ISBN 0-47139698-2.
- [6] Chen B, Dingerdissen U, Krauter JGE, Lansink Rotgerink HGJ, Möbus K, Ostgard DJ, Panster P, Riermeir TH, Seebald S, Tacke T, Trauthwein H. New developments in hydrogenation catalysis particularly in synthesis of fine and intermediate chemicals. *App. Catal. A: Gen.* 2005; 280: 17–46. DOI: 10.1016/j.apcata.2004.08.025.
- [7] Lindlar H, Dubuis R, Jones FN, McKusick BC. Palladium catalyst for partial reduction of acetylenes. *Org. Synth.* 1966; 46: 89–92.
- [8] Anderson JA, Mellor JL, Wells RPK. Pd catalysed hexyne hydrogenation modified by Bi and by Pb. *J. Catal.* 2009; 261: 208–216. DOI: 10.1016/j.jcat.2008.11.023.
- [9] Evangelisti C, Panziera N, D'Alessio A, Bertinetti L, Botavina M, Vitulli G. New monodispersed palladium nanoparticles stabilized poly-(N-vinyl-2-pyrrolidone): Preparation, structural study and catalytic properties. *J. Catal.* 2010; 272: 246–252. DOI: 10.1016/j.jcat.2010.04.006.
- [10] Radovic LR, Rodríguez-Reinoso F. Carbon Materials in Catalysis. In *Chemistry and Physics of Carbon*. Thrower PA, 14 Ed., Marcel Dekker: New York, NY; 1996, Vol. 25, p. 243. ISBN 9780824793685
- [11] Salinas-Martínez de Lecea C, Linares-Solano A, Díaz-Auñón JA, L'Argentièrre PC. Improvement of activity and sulphur resistance of Pd complex catalysts using carbon-coated γ -Al₂O₃ and activated carbon supports. *Carbon* 2000; 38: 157–160. DOI: 10.1016/S0008-6223(99)00230-4.
- [12] Lederhos CR, Badano JM, Quiroga ME, Coloma-Pascual F, L'Argentièrre PC. Influence of Ni addition to a low-loaded palladium catalyst on the selective hydrogenation of 1-heptyne. *Quim. Nova.* 2010; 33(4): 816–820.
- [13] Quiroga M, Liprandi D, Cagnola E, L'Argentièrre P. 1-heptyne semihydrogenation catalyzed by palladium or rhodium complexes. Influence of: metal atom, ligands and the homo/heterogeneous condition. *Appl. Catal. A: Gen.* 2007; 326: 121–129. DOI: 10.1016/j.apcata.2007.03.035.
- [14] Lennon D, Marshall R, Webb G, Jackson SD. The effect of hydrogen concentration on propyne hydrogenation over a carbon supported palladium catalyst studied under continuous flow conditions. *Stud. Surf. Sci. Catal.* 2000; 130: 245–250.
- [15] Hamilton CA, Jackson SD, Kelly GJ, Spence R, de Bruin D. Competitive reactions in alkyne hydrogenation. *App. Catal. A: Gen.* 2002; 237: 201–209. DOI: 10.1016/S0926-860X(02)00332-0.

- [16] Díaz-Auñón JA, Román-Martínez MC, L'Argentièrre PC, Salinas-Martínez de Lecea C. Catalytic lifetime of amine metal complexes supported on carbons in cyclohexene hydrogenation. *Stud. Surf. Sci. Catal.* 2000; 130C: 2075–2080. DOI: 10.1016/S1381-1169(99)00355-6.
- [17] Díaz-Auñón JA, Román-Martínez MC, Salinas-Martínez de Lecea C, L'Argentièrre PC, Cagnola EA, Liprandi D, Quiroga ME. $[\text{PdCl}_2(\text{NH}_2(\text{CH}_2)_{12}\text{CH}_3)_2]$ supported on an active carbón: effect of the carbon properties on the catalytic activity of cyclohexene hydrogenation. *J. Mol. Catal. A: Chem.* 2000; 153: 243–256. DOI: 10.1016/S1381-1169(99)00355-6.
- [18] Wang C-B, Lin H-K, Ho C-M. Effects of the addition of titania on the thermal characterization of alumina-supported palladium. *J. Mol. Catal. A: Chem.* 2002; 180: 285–291. DOI: 10.1016/S1381-1169(01)00450-2.
- [19] Lederhos C, L'Argentièrre PC, Fígoli NS. 1-Heptyne selective hydrogenation over Pd supported catalysts. *Ind. Eng. Chem. Res.* 2005; 44: 1752–1756.
- [20] Liprandi DA, Quiroga ME, Cagnola EA, L'Argentièrre PC. A new more sulfur-resistant rhodium complex as an alternative to the traditional Wilkinson's catalyst. *Ind. Eng. Chem. Res.* 2002; 41: 4906–4910.
- [21] Li L, Zhu ZH, Yan ZF, Lu GQ, Rintoul L. Catalytic ammonia decomposition over Ru/carbon catalysts: The importance of the structure of carbon support. *Appl. Catal. A: Gen.* 2007; 320: 166–172. DOI: 10.1016/j.apcata.2007.01.029.
- [22] Gaspar AB, Dieguez LC. Dispersion stability and methylcyclopentane hydrogenolysis in Pd/ Al_2O_3 catalysts. *Appl. Catal. A: Gen.* 2001; 201: 241–251. DOI: 10.1016/S0926-860X(00)00442-7.
- [23] L'Argentièrre PC, Cañón MM, Fígoli NS, Ferrón. AES and XPS studies of the influence of Ni addition on Pd/ Al_2O_3 catalytic activity and sulfur resistance. *J. Appl. Surf. Sci.* 1993; 68: 41–47. DOI: 10.1016/0169-4332(93)90214-V.
- [24] NIST X-ray Photoelectron Spectroscopy Database NIST Standard Reference Database 20, Version 3.5 (Web Version), National Institute of Standards and Technology, USA; 2007.
- [25] Pârvulescu VI, Filoti G, Pârvulescu V, Grecu N, Angelescu E, Nicolescu IV. Styrene hydrogenation on supported Pd, Fe and Pd-Fe/ γ - Al_2O_3 catalysts. *J. Mol. Catal.* 1994; 89: 267–282. DOI: 10.1016/0304-5102(93)E0312-5.
- [26] Abu Bakar NHH, Bettahar MM, Abu Bakar M, Monteverdi S, Ismail J. Low temperature activation of Pt/Ni supported MCM-41 catalysts for hydrogenation of benzene. *J. Mol. Catal. A: Chem.* 2010; 333: 11–19. DOI: 10.1016/j.molcata.2010.10.007.
- [27] Álvarez-Rodríguez J, Rodríguez-Ramos I, Guerrero-Ruiz A, Arcoya. A Selective hydrogenation of citral over Pt/KL type catalysts doped with Sr, La, Nd and Sm. *Appl. Catal. A: Gen.* 2011; 401: 56–64. DOI: 10.1016/j.apcata.2011.04.045.

- [28] Hillebrecht FU, Fuggle JC, Bennett PA, Zolnierrek Z. Electronic structure of Ni and Pd alloys. II. X-ray photoelectron core-level spectra. *Phys. Rev. B* 1983; 27: 2179–2193.
- [29] Kennedy DR, Webb G, Jackson SD, Lennon D. Propyne hydrogenation over alumina-supported palladium and platinum catalysts. *Appl. Catal. A: Gen.* 2004; 259: 109–120. DOI: 10.1016/j.apcata.2003.09.018.
- [30] Wang C-B, Lin H-K, Ho C-M. Effects of the addition of titania on the thermal characterization of alumina – supported palladium. *J. Molec. Catal. A: Chem.* 2002; 180: 285–291. DOI: 10.1016/S1381-1169(01)00450-2.
- [31] Mukainakano Y, Yoshida K, Okumura K, Kunimori K, Tomishige K. Catalytic performance and QXAFS analysis of Ni catalysts modified with Pd for oxidative steam reforming of methane. *Catal. Today* 2008; 132: 101–108. DOI: 10.1016/j.cattod.2007.12.031.
- [32] Li G, Hu L, Hill JM. Comparison of reducibility and stability of alumina-supported Ni catalysts prepared by impregnation and co-precipitation. *Appl. Catal. A: Gen.* 2006; 301: 16–24. DOI: 10.1016/j.apcata.2005.11.013.
- [33] Hou Z, Yokota O, Tanaka T, Yashima T. Characterization of Ca-promoted Ni/ α -Al₂O₃ catalyst for CH₄ reforming with CO₂. *Appl. Catal. A: Gen.* 2003; 253: 381–387. DOI: 10.1016/S0926-860X(03)00543-X.
- [34] Abelló S, Verboekend D, Bridier B, Pérez-Ramírez J. Activated takovite catalysts for partial hydrogenation of ethyne, propyne, and propadiene. *J. Catal.* 2008; 259: 85–95. DOI: 10.1016/j.jcat.2008.07.012.
- [35] Hoffer BW, van Langeveld AD, Janssens JP, Bonné RLC, Lok CM, Moulijn JA. Stability of highly dispersed Ni/Al₂O₃ catalysts: effects of pretreatment. *J. Catal.* 2000; 192: 432–440. DOI: 10.1006/jcat.2000.2867.
- [36] Dias JAC, Assaf JM. Autothermal reforming of methane over Ni/ γ -Al₂O₃ promoted with Pd. The effect of the Pd source in activity, temperature profile of reactor and in ignition. *Appl. Catal. A* 2008; 334: 243–250. DOI: 10.1016/j.apcata.2007.10.012.
- [37] Coq B, Figueras F. Bimetallic palladium catalysts: influence of the co-metal on the catalyst performance. *J. Mol. Catal A: Chem.* 2001; 173: 117–134. DOI: 10.1016/S1381-1169(01)00148-0.
- [38] Mallat T, Baiker A. Selectivity enhancement in heterogeneous catalysis induced by reaction modifiers. *Appl. Catal. A: Gen.* 2000; 200: 3–22. DOI: 10.1016/S0926-860X(00)00645-1.
- [39] Nijhuis TA, van Koten G, Moulijn JA. Optimized palladium catalyst systems for the selective liquid-phase hydrogenation of functionalized alkynes. *Appl. Catal. A: Gen.* 2003; 238: 259–271. DOI: 10.1016/S0926-860X(02)00372-1.
- [40] Lederhos C, L'Argentièrre PC, Coloma-Pascual F, Fígoli NS. A study about the effect of the temperature of hydrogen treatment on the properties of Ru/Al₂O₃ and Ru/C and

their catalytic behavior during 1-heptyne semi-hydrogenation. *Catal. Lett.* 2006; 110: 23–28. DOI: 10.1007/s10562-006-0085-z.

- [41] L'Argentièrè PC, Cagnola EA, Quiroga ME, Liprandi DA. A palladium tetra-coordinated complex as catalyst in the selective hydrogenation of 1-heptyne. *Appl. Catal. A: Gen.* 2002; 226: 253–263. DOI: 10.1016/S0926-860X(01)00911-5.
- [42] Liprandi DA, Cagnola EA, Quiroga ME, L'Argentièrè PC. Influence of the reaction temperature on the 3-hexyne semi-hydrogenation catalyzed by a palladium(II) complex. *Catal. Lett.* 2009; 128: 423–433. DOI: 10.1007/s10562-008-9768-y.
- [43] Mouaddib M, Perrichon V. Influence of the support in the alcohols synthesis. In *Proceedings of the 9th International Congress on Catalysis*. Phillips MJ, Ternant M, Eds., The Chemical Institute of Canada: Ottawa, Canada; 1988, Vol. 2, p. 521.
- [44] Shriver DF, Atkins PW, Langford CH. *Inorganic Chemistry*, 3rd edn. WH Freeman and Co., New York, NY; 1994, p. 258.