Hept-1-yne partial hydrogenation reaction over supported Pd and W catalysts

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ABSTRACT

In order to increase the production of olefins the partial hydrogenation of alkynes has achieved industrial importance. In this sense catalysts with selective hydrogenation properties may be of potential interest. In this work mono and bimetallic Pd and W catalysts supported on γ-alumina with low metal content (2.4% W and 0.4% Pd) were prepared. XPS, XRD, TPR and hydrogen chemisorption techniques were used for the characterization. The effect of metallic precursor incorporation order and of the reduction temperature, on the activity and selectivity for the partial hydrogenation of hept-1-yne at mild reaction conditions, were evaluated.

Low-loaded palladium monometallic catalyst showed a high selectivity but it was the least active. Moreover, bimetallic catalysts proved to be more active than the classical Lindlar catalyst. The addition of Pd to the W/γ-Al$_2$O$_3$ catalyst greatly improved the total conversion and the selectivity to the desired product. XPS results suggest electronic effects between Pd and W metals. The bimetallic W-Pd catalyst treated in hydrogen at low temperature conditions (393 K) showed the highest activity and selectivity values.

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1. Introduction

The partial hydrogenation of acetylenes using homogeneous and heterogeneous catalysts has been broadly studied in the last years due to its academic and industrial interest [1,2]. The partial transformation of the alkyne to the corresponding alkene is possible because the alkyne is more strongly bonded to the metal, thus competing for the active sites, displacing the alkene and limiting its readsorption for further hydrogenation. Numerous products obtained from these partial hydrogenation reactions are useful in the synthesis of biologically active compounds [3], the production of margarine, the lubricant industry and the synthesis of important intermediates for the fine chemicals industry [4].

Many authors have found that palladium supported catalysts exhibit the best catalytic properties in the partial hydrogenation reactions of alkynes and dienes to olefins. High loaded Pd catalysts (≥1 wt%) have both high activity and selectivity [5–7]. The addition of a second metal to Pd monometallic catalysts has also been found to improve the catalytic properties in several reactions. These so-called bimetallic catalysts have improved activity, selectivity and stability. Many authors have reported the effect of this second metal on the performance of palladium-based bimetallic catalysts [8–10]. The most clear example is the well-known Lindlar catalyst, Pd$_{(5\%)}$/CaCO$_3$ modified with lead, used for the selective hydrogenation of alkynes. This catalyst has been studied since 1954 [11]. Many authors have studied the addition of metals (Ni, Ag, Cu, Au, Ge, Sn, Pb, etc.) to monometallic palladium catalysts and several supports have been tried (γ-Al$_2$O$_3$, zeolites, silica, etc.) [8,10,12–16]. Though these catalysts proved to be active for partial hydrogenation, all the studies were concentrated on the reaction of short chain terminal alkynes. There are however only scarce reports that deal with the selective hydrogenation of long chain alkynes [17–20]. In a recent work, different low-loaded Pd, Ni and Pd-Ni catalysts were tested for the partial hydrogenation of hept-1-yne, a high molecular weight terminal alkyne [21]. It was found that the Pd$_{0.4\%}$-Ni$_{1\%}$ bimetallic catalyst was more active than the Pd monometallic catalyst while both catalysts were very selective for the production of hept-1-ene (>95%). These catalysts were however less active than the commercial Lindlar catalyst.

Surface anchored tungsten oxide is well known as an effective catalyst for several acid-catalyzed reactions, such as the skeletal isomerization and polymerization of olefins, the dehydration and esterification of alcohols, hydrodenitrogenation reactions, etc. [22–24]. In general most authors have studied supported tungsten

catalysts, mono or bimetallic, with high metal contents on several reactions [24–26]. Sica and Gigola [27] found high tungsten losses due to the volatility of some oxidized species. Tungsten losses could be minimized using smaller tungsten contents. However it has also been found that the presence of well dispersed WO$_3$ on alumina during the synthesis of bimetallic catalysts prevents the W–(noble metal) interaction and as a result the reducibility of W becomes greatly inhibited. For this reason several authors have proposed that in order to reduce the volatility and increase the reducibility of WO$_x$ species, special preparation procedures must be devised in order to put tungsten species in intimate contact with the noble metal [27–29]. To our knowledge, there are no reports about the use of supported tungsten in monometallic or bimetallic catalysts for the selective hydrogenation of alkynes.

Based on the above considerations the objectives of this work have been: (a) to prepare low metal content catalysts based on Pd and W; (b) to evaluate the effects of precursor impregnation sequence, (c) to study the effect of the pretreatment reduction temperature on the activity and selectivity during hept-1-yne partial hydrogenation at mild reaction conditions; (d) to compare these catalysts with commercial Lindlar catalyst.

2. Experimental

2.1. Catalyst preparation

γ-Al$_2$O$_3$ Ketjen CK 300 was used as support. This was previously calcined in air at 823 K to stabilize its texture (S_{BET}: 180 m^2 g^{-1}, cylindrical pellets of 1.5 mm diameter). Palladium and tungsten monometallic catalysts and W-Pd and Pd-W bimetallic catalysts supported over alumina were prepared by the incipient wetness technique. Volume and concentration of the impregnating solutions were adjusted to get 0.4 wt% Pd and 2.4 wt% W on the final mono and bimetallic catalysts.

An aqueous acid solution of Pd(NO$_3$)$_2$ (Fluka, Cat. No. 76070) at pH 1 (with HNO$_3$) was used to prepare the palladium monometallic catalyst (sample PdAl). The tungsten monometallic catalyst (sample WAl) was prepared using a phosphotungstic acid solution H$_3$PO$_4$·12WO$_3$ (Fluka, Cat. No. 79690). After impregnation both monometallic catalysts were dried overnight at 373 K and calcined in an air flow at 823 K for 3 h [30]. A portion of WAl was impregnated with an aqueous acid solution of Pd(NO$_3$)$_2$ (pH 1 with HNO$_3$) to obtain the bimetallic catalyst named WPd. On the other hand, part of the PdAl catalyst batch was impregnated with an aqueous acid solution of H$_3$PO$_4$·12WO$_3$ to prepare the bimetallic catalyst labeled PdW. These bimetallic catalysts (WPd and PdW) were dried and calcined in an air flow at the same conditions described above for the monometallic catalysts.

Before its catalytic evaluation the tungsten and palladium monometallic catalysts (WAl and PdAl) were reduced in a hydrogen stream during 1 h at 673 and 573 K, respectively. The bimetallic catalysts (WPd and PdW) were reduced at different temperatures (393, 573 and 773 K) for 1 h. These catalysts were called WPd_T(K) and PdW_T(K). T(K) is the reduction temperature in Kelvin degrees. All the catalysts were immediately used in the tests reaction after the reduction treatment.

The commercial Lindlar catalyst, 5% Pd on calcium carbonate and poisoned with Pd, was provided by Aldrich (Cat. No. 20,573-7) and was used without any pretreatment for comparative purposes as suggested by other authors for alkyne hydrogenation reactions [31].

2.2. Catalyst characterization

Palladium, tungsten and phosphorous contents were determined by inductively coupled plasma analysis (ICP) in an OPTIMA 21200 Perkin Elmer equipment.

The hydrogen chemisorption of the metal particles on the catalysts surface was measured at 303 K in a Micromeritics AutoChem II 2920 instrument equipped with a thermal conductivity detector (TCD). 0.2 g of the samples were reduced *in situ* in a 5% (v/v) hydrogen/argon stream during 1 h at the same reduction temperature used before each catalytic test. This methodology ensures that the results of chemisorption are not masked by the formation of β-PdH phase. The samples were degassed *in situ* in an argon flow (AGA, 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 chemisorption stoichiometry H:M = 1 (M: Pd or W) [32].

The electronic states of surface species were determined by X-ray Photoelectron Spectroscopy (XPS) in a VG-Microtech Multilab equipment, equipped with a MgKα ($h\nu$: 1253.6 eV) radiation and a pass energy of 50 eV. The analysis pressure during data acquisition was 5×10^{-7} Pa. Samples were treated *in situ* in the presence of a H$_2$ stream following the same pretreatment conditions for each catalyst. A careful deconvolution of the spectra was made and the areas under the peaks were estimated by calculating the integral of each peak after subtracting a Shirley background and fitting the experimental peak to a combination of Lorentzian/Gaussian lines of 30–70% proportions. The reference binding energy (BE) was C 1s peak at 285.0 eV.

X-ray diffraction (XRD) measurements of powdered samples were obtained using Shimadzu XD-D1 instrument with a CuKα radiation (λ = 1.5405 Å) in the 21 < 2θ < 49° at a scan speed of 0.25° min^{-1}. Samples were powdered and reduced under a hydrogen flow, the samples were put into the chamber of the equipment and then data acquisition was made.

The reducibility of the surface species in all the catalysts were determined by Temperature Programmed Reduction (TPR), using a Micromeritics AutoChem II instrument equipped with a TCD. Samples were pretreated under an oxygen flow stream at 673 K during 30 min, and then they were cooled down room temperature under an argon flow. 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.

2.3. Catalytic evaluations

Catalytic reaction tests were carried out in a stainless steel stirred tank batch reactor equipped with a magnetically coupled stirrer with two blades in counter-rotation that was operated at 750 rpm. The inner wall of the reactor was completely coated with PTFE in order to prevent the catalytic action of steel reported by other authors [33]. Catalyst samples of 0.75 g, a temperature of 303 K and a hydrogen pressure of 150 kPa were used. The reactant hept-1-yne (Fluka, Cat. No. 51950, >98%) was dissolved to a 5% (v/v) in toluene (Merck, Cat. No. TX0735-44, >99%). The reactant:palladium molar ratio used was 1100 for all the catalysts. The possible diffusional limitations during the catalytic tests were assessed following a procedure previously described [34]. Experiments were carried out at different stirring velocities in the 180–1400 rpm range. Stirring velocities higher than 500 rpm allowed to obtain for all the catalysts, identical values of activity and selectivity. This fact ensures that external diffusional limitations were absent at the selected speed (750 rpm). To further ensure that the catalytic results were not influenced by external and intraparticle mass transfer limitations, the catalyst particles were crushed up to 1/4 of their original size. Then several runs using the crushed catalysts were made. In every run the conversion and selectivity values of the crushed catalysts were the same (within experimental error) as those of the non-crushed catalyst. Therefore it can be inferred that internal diffusional limitations were absent in the reaction conditions of this work.

Table 1

Metal loading, Hydrogen chemisorption capacity ($H_{2\,chem}$), W $4f_{7/2}$ binding energies (BE), degree of reduction of palladium (Pd_{red}/Pd_{total}) and maximum yield of hep-1-ene (Y^M).

Catalysts	Metal loading		$H_{2\,chem}$ ($\mu mol_{H2}\,g_{cat}^{-1}$)	W $4f_{7/2}$ BE (eV)	Pd_{red}/Pd_{total} (%)	Y^M (%)
	Pd (wt%)	W (wt%)				
WAl	–	2.37	n.d.	36.1	–	23.0[a]
WPd_393	0.41	2.37	10	35.0	52.0	95.0[a]
WPd_573	0.41	2.37	12	35.7	52.0	78.5[a]
WPd_773	0.41	2.37	16	36.0	52.0	50.3[a]
PdAl	0.38	–	18	–	99.0	17.6[b]
PdW_393	0.38	2.42	15	35.0	57.8	55.0[b]
PdW_573	0.38	2.42	11	35.3	57.8	55.0[b]
PdW_773	0.38	2.42	n.d.	35.6	57.8	58.5[b]
Lindlar	5	–	–	–	–	52.0[a]

n.d.: no hydrogen consumption was detected.
Corresponding reaction time (a) 180 min; (b) 150 min.

Catalytic tests were carried out in triplicates with an experimental error lower than 3%. Reactants and products were analyzed by gas chromatography using a flame ionization detector and an HP InnoWax polyethyleneglycol capillary column (30 m long, 0.32 mm ID).

3. Results and discussion

ICP chemical analysis confirmed the metal loading of each catalyst, within a 5% error, which was considered negligible; these values are shown in Table 1.

Phosphorus combines directly with all metals (except Bi, Hg, Pb) with a very varied stereochemistry and bonding, acting as a Lewis base center with possibility of "valence expansion", which is the ability of 3d orbital for bonding [35]. After the impregnation of the phosphotungstic acid solution over the support, it is necessary to remove the elemental phosphorous in order to avoid the poisoning of the palladium metallic centers. Some researchers have found that the pre-treatment of WAl catalyst in the presence of an air flow at 823 K during 3 h is enough to eliminate all the phosphorous from the monometallic catalyst [30,36]. After the calcination and reduction of the prepared catalysts, no phosphorous was detected by ICP chemical analysis. This result indicates that after the calcination all phosphorus was eliminated from the catalysts.

Also, Table 1 shows the hydrogen chemisorption capacities of the catalysts ($H_{2\,chem}$). For the monometallic WAl catalyst the consumption of hydrogen was not detected during the chemisorption analysis. For this reason for the bimetallic catalysts we considered that only the palladium sites were responsible for the hydrogen chemisorption. For the bimetallic WPd catalysts the values of hydrogen consumption considerably increased with reduction temperature. Whereas the PdW catalysts the hydrogen consumption decreased dramatically as the reduction temperature was increased. Indeed for the PdW_773 sample no consumption of H_2 was detected. The hydrogen consumption values found could indicate that in the WPd series Pd is more accessible to hydrogen chemisorption than in the PdW series. This could be due to an effect of decoration of Pd particles by W species [30]. Sica and Gigola [27] have reported this effect for Pd-WO$_x$/Al$_2$O$_3$ catalysts with low metal content. The possible decoration of Pd particles by WO$_x$ species is an example of metal–support interaction related to the mobility of support surface species. Surface species would migrate onto Pd particles during heat treatments. The mobility is only important at high temperatures.

Because of the low concentration of palladium in all samples the signal-to-noise ratio during the measurement of the Pd $3d_{5/2}$ binding energies by XPS was very low. For this reason these results were considered not reliable enough and no conclusions were tried to be drawn from them. Fig. 1 shows the XPS spectra (BE of W $4f_{7/2}$)

for WAl and bimetallic WPd (Fig. 1A) and for WAl and bimetallic PdW (Fig. 1B) at the different reduction temperatures. The maximum binding energy (BE) of the peaks of W $4f_{7/2}$ of all the samples is also listed in Table 1. According to the literature the BE of W $4f_{7/2}$ in the case of metallic tungsten W^0 appears at 34.0 eV [37]. The WAl monometallic catalyst reduced at 673 K had its W $4f_{7/2}$ signal at 36.1 eV. According to a previous work [23], this value of BE indicates that tungsten is present on the alumina surface as an electron-deficient species, W^{6+}, after calcination and reduction [37]. As shown in Fig. 1A and in Table 1, the WPd bimetallic catalysts had W $4f_{7/2}$ peaks at 35.0, 35.7 and 36.0 eV when they were
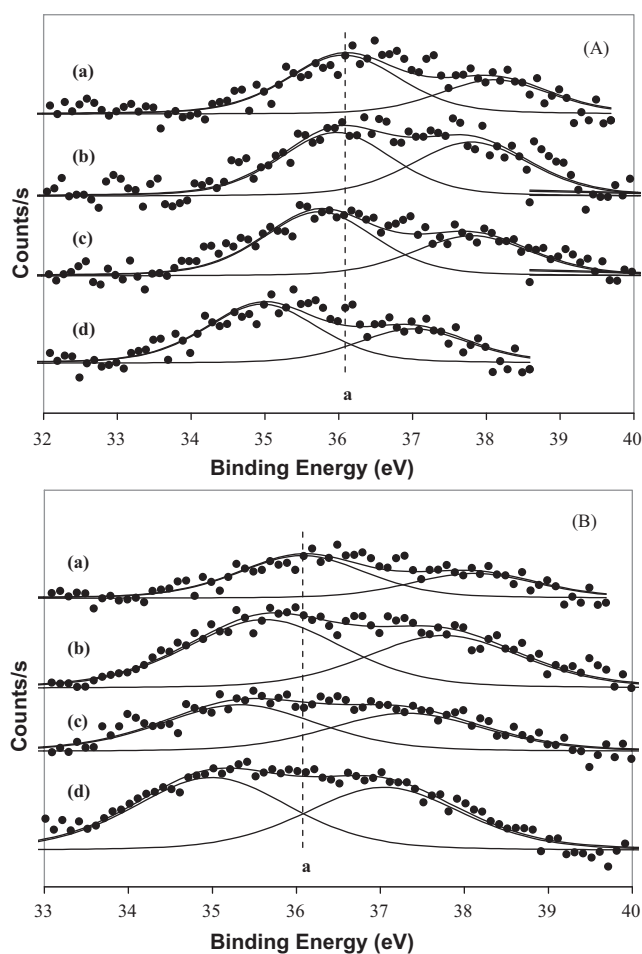
Fig. 1. XPS W $4f_{7/2}$ spectra for: (A) WAl and WPd samples. (B) WAl and PdW samples. Where: WAl (a), T(K): 773 (b), 573 (c) and 393 (d).
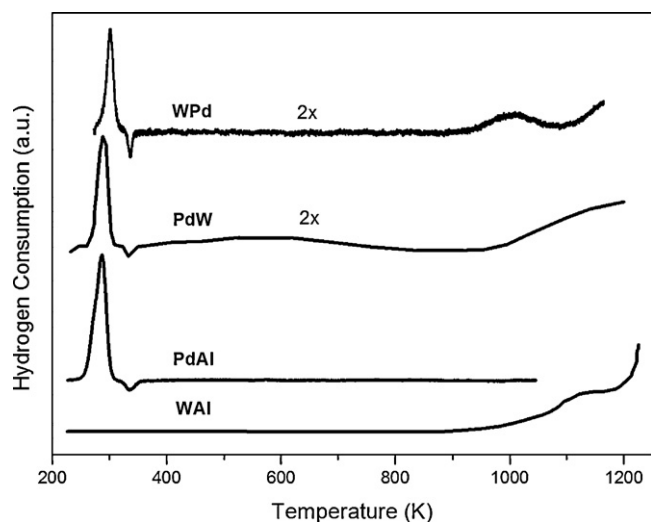
Fig. 2. TPR traces of WAl, PdAl, PdW and WPd samples.

reduced at 393, 573 and 773 K, respectively. According to currently literature this BEs can be due to the presence of surface electron-deficient species [23,32,37–39]. It can also be seen that as the reduction temperature of the WPd bimetallic catalysts is increased, the tungsten becomes more electron-deficient (Fig. 1A). The same pattern is seen in the case of the PdW bimetallic catalysts (Fig. 1B). For this series values of the W $4f_{7/2}$ BE of 35.0, 35.3 and 35.6 eV were recorded for the catalysts reduced at 393, 573 and 773 K, respectively. In these bimetallic catalysts the presence of surface W^{6+} species is also found after the thermal treatments. The BE showed in Table 1 indicate that the most electron-deficient specie of tungsten is obtained on the monometallic WAl catalyst. All the bimetallic catalysts (PdW or WPd) presented lower values of BE than the tungsten monometallic catalyst (WAl). All the bimetallic catalysts (PdW or WPd) presented lower values of BE than the tungsten monometallic catalyst (WAl). This pattern can be explained due to an electron transfer from the d orbitals of Pd to the f orbitals of W rather than the formation of Pd–W bond. This electron transfer decrease as the reduction temperature is increased. This transfer might be due to the formation of intermediate Pd–W–Al_2O_3 surface species. Similar results were found by other authors [30].

For the Lindlar catalyst the BE of the Pd $3d_{5/2}$ signal was 337.2 eV. This indicates that Pd in this catalyst is electron-deficient (Pd^{n+} with $0 < n < +2$) [37].

For all the samples the obtained difractograms only presented the typical signals of the gamma phase of alumina: 37.7°, 45.98° and 66.98° [40,41]. For this reason the difractograms are not presented. With respect to the presence of Pd crystallites, these are undetectable because of the low amount of Pd on the catalysts (0.4 wt%) that is well below the detection limit of this technique. The absence of peaks in the region $20° < 2\theta < 30°$ indicates that there is no tungsten oxide present as a crystalline segregated phase. Segregated monoclinic WO_3 crystallites can be detected by XRD for W surface concentrations higher than the corresponding surface saturation value (4.3 W atoms nm^{-2}) [42]. In our case, the W surface density was lower than the corresponding monolayer value (0.44 W atoms nm^{-2}). Due to the low W loading used in our case the presence of crystalline species was not expected [22].

The TPR traces of the palladium and tungsten catalysts (mono and bimetallic) are shown in Fig. 2 According to the available literature [43] based on TPR tests of WO_3-Al_2O_3 samples high temperatures are needed in order to reduce tungsten oxides (WO_x) to W^0. For tungsten loading of 15 wt%, Busto et al. [44] suggested that during reduction of tungsten oxides in hydrogen sreams, a series of

four reduction stages occur: (a) between 573 and 773 K, WO_3 would be converted to substoichiometric $WO_{2.9}$, (b) this compound would be converted into WO_2 between 823 and 973 K, (c) the reduction of WO_2 to W^0 would take place in the 1023–1123 K range, and (d) at higher temperatures, in the 1173–1223 K range, the reduction of WO_x species with strong interaction with the support would occur. For W loadings below the monolayer value (as it is our case) there would be only W species with a strong interaction with the support and this interaction would have a marked influence on the reduction pattern. For this reason the reducibility of tungsten supported on alumina is more difficult when the tungsten loading is low [22].

Fig. 2 shows the TPR trace of the W monometallic catalyst. A main peak of reduction starting at 900 K and a shoulder at 1143 K can be seen. The maximum hydrogen consumption occurs at temperatures higher than 1220 K. This is in agreement with other data reported by Contreras et al. [43], who reported TPR traces of WO_x species on alumina with reduction peaks at high temperatures, between 950 and 1300 K that could be attributed to the reduction of highly dispersed WO_x bound to alumina through strong bonds. In the same way, Cruz et al. [25] reported a main peak of W reduction at 1323 K in the case of the TPR test of WO_3-Al_2O_3 catalysts. This was attributed to the reduction of WO_x to W. Logie et al. [45] indicated that peaks at 1073 K can be assigned to the reduction to the metal state of amorphous species of tungsten oxide grafted on alumina and of tungsten oxide species of stoichiometry WO_{3-x} ($0 < x < 1$). Therefore, according to the literature reports for those catalysts with submonolayer W loading, the high temperature peak above 1000 K can be attributed to the reduction of amorphous WO_x species.

The TPR trace of the Pd monometallic catalyst had a main hydrogen consumption peak at a low temperature (287 K). This peak can be attributed to the reduction of PdO species and to the formation of palladium hydrides [46,47]. This catalyst also has an inverted reduction peak at 339 K that could be related to the decomposition of the β-PdH phase [32,48]. These species interact weakly with the support and therefore Pd can be easily reduced. Reduction can indeed proceed completely at room temperature in a hydrogen atmosphere [49].

Fig. 2 shows the TPR traces of the WPd and PdW catalysts. At low temperatures they have a reduction pattern very similar to the PdAl one. A main peak of reduction is seen at 284 K or 290 K that can be attributed to the reduction of PdO and to the formation of the β-PdH phase. The inverted peak of decomposition of this hydride phase can also be found at 332 K and 335 K. In the bimetallic catalysts the presence of W slightly modifies the position of the Pd reduction peak (see the PdAl trace for comparison) but modifies the peak height. The high temperature peaks (>950 K) are similar to those found in the case of the monometallic WAl catalyst at high temperatures (>1200 K) [27,50] and would therefore be related to the reduction of amorphous oxidized W species.

It must be noted that according to the TPR tests Pd on the mono and bimetallic catalysts (PdAl, WPd or PdW) is, at least in part, in the Pd^0 metal state after the reduction treatment used before the catalytic tests.

The degrees of reduction of the mono and bimetallic catalysts (Pd_{red}/Pd_{total}, reduced metal amount to total metal amount ratio) were determined by integration of the TPR trace, using a stoichiometry of reduction of one ($H_2/Pd^{2+} = 1$), and are shown in Table 1. The values of (Pd_{red}/Pd_{total}) of the monometallic PdAl catalysts indicate that Pd is mostly reduced (99%) while in PdW and WPd is only moderately reduced (57.8% and 52%, respectively). This difference could be attributed to a possible decoration of Pd particles by WO_x species. This possible decoration of Pd particles by WO_x species would produce two consequences: a decrease of the accessible surface Pd sites (geometric effect) and an increase of electronic interaction between Pd atoms and W and O atoms (elec-
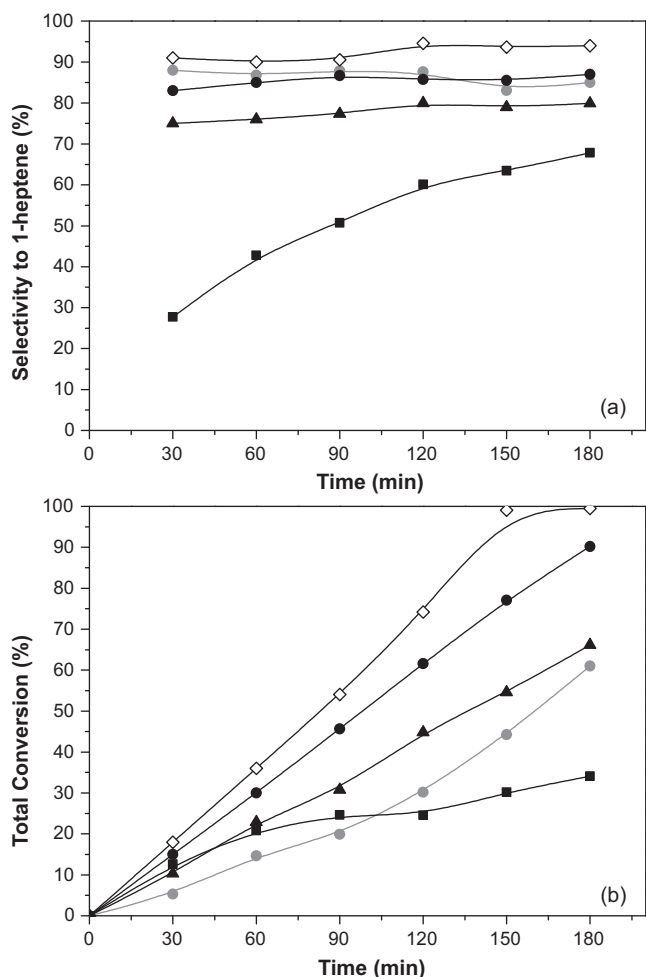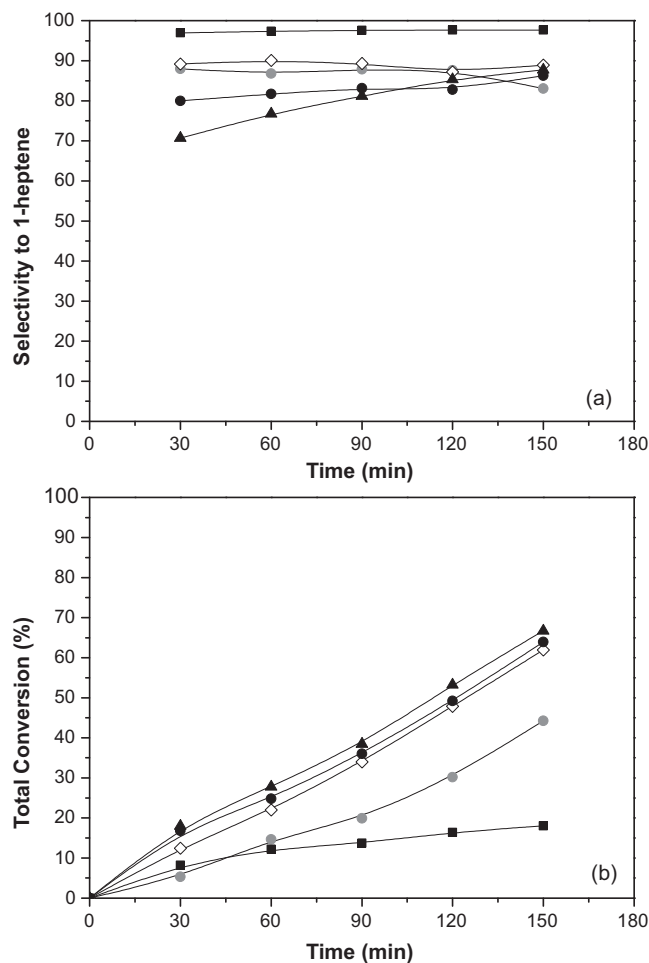
Fig. 3. Hept-1-yne reaction test (303 K, 150 kPa) results. (a) selectivity to hept-1-ene (%) and (b) total conversion (%) as a function of reaction time. WAl (■); WPd_393K (◇); WPd_573K (●); WPd_773K (▲); Lindlar (●).

Fig. 4. Hept-1-yne reaction test (303 K, 150 kPa) results. (a) selectivity to hept-1-ene (%)and (b) total conversion (%) as a function of reaction time. PdAl (■); PdW_393K (◇); PdW_573K (●); PdW_773K (▲); Lindlar (●).

tronic effect). Both effects might be responsible for the decrease in the hydrogen consumption in TPR and hydrogen chemisorption capacity, while the second should be reflected in the appearance of electron-deficient Pd or W. Nevertheless the modification in the position of the reduction peak of Pd would be indicative of a decorative effect of electron-deficient W species with Pd particles. This effect is more marked at higher reduction temperatures.

During the catalytic test the only reaction products observed were hept-1-ene and n-heptane. Figs. 3 and 4 show the values of total conversion of hept-1-yne and selectivity to hept-1-ene as a function of reaction time for the different mono and bimetallic catalysts and the reference Lindlar catalyst.

In both Figures it can be seen that the monometallic WAl catalyst is an active system for the hydrogenation of hept-1-yne. Fig. 3a shows that WAl had the lowest selectivity to hept-1-ene in comparison to the bimetallic WPd catalysts. The addition of Pd to the tungsten monometallic catalyst greatly improves the selectivity to the desired product. However this improvement is found to decrease with the increase in the reduction temperature. The rank of alkene selectivity values found was: $S_{WPd\_393} > S_{WPd\_573} > S_{WPd\_773}$. The figure also shows that the selectivity of the commercial Lindlar catalyst was lower than 90%.

Fig. 3b clearly shows that for reaction times lower than 90 min the reaction proceeds like a zero order one for all the catalyst. It can also be seen that as the reduction temperature is increased the total conversion of hept-1-yne is decreased. The

commercial Lindlar catalyst has lower values of total conversion than bimetallic WPd. The bimetallic WPd catalyst reduced at the lowest temperature (393 K) achieves full conversion (100%) of hept-1-yne after 150 min of reaction while the commercial Lindlar catalysts only reaches 45% of hept-1-yne total conversion. It is noteworthy convenient to remark that after reducing the bimetallic WPd catalyst at 393 K the selectivity obtained in the reaction is higher than the corresponding to the Lindlar catalyst (>90%).

The high selectivity of the Pd monometallic catalyst observed in Fig. 4 is remarkable. The addition of W to PdAl decreases the values of selectivity to the desired products. It can also be seen that as the reduction temperature is increased the selectivity of the PdW catalysts is decreased. However it must be noted that the variation of the reduction temperature only affects the selectivity values in the 0–120 min time of reaction range. At higher time values, the selectivities of the bimetallic catalysts and the Lindlar catalyst are very similar. PdAl shows higher values of selectivity and a low total conversion (<20%). The addition of tungsten to this catalyst increases the conversion 3.5 times. For this catalyst the total conversion is only slightly affected by the variation in the reduction temperature.

It must be noted that the reference catalyst (Lindlar) has a high selectivity to the formation of the desired alkene all throughout the reaction test. This selectivity value is lower than that obtained with the WPd_393 catalyst and similar to those obtained with the WPd_573 and PdW_393 K catalysts (Fig. 3a). It is important to remark that, at the same reaction time, all bimetallic catalysts (PdW

and WPd) had a higher activity than the Lindlar catalyst (see Figs. 3b and 4b).

Table 1 also contains the values of maximum yield to hept-1-ene (Y^M) and the corresponding reaction times at which these maxima were found. The results indicate that the WPd_393 catalyst is the best for hydrogenation of hept-1-yne. All the prepared bimetallic catalysts produced higher yields of hept-1-ene than the reference Lindlar catalyst. It can be therefore concluded that the addition of a second metal to a monometallic W or Pd catalyst greatly improves the catalytic activity and selectivity for partial hydrogenation of hept-1-yne. The thus formed WPd catalysts synthetized in this work have a better performance than the commercial Lindlar catalysts for this kind of reactions. The pretreatment with hydrogen at low temperatures enhances the catalytic properties of the bimetallic WPd and PdW catalysts. Then these catalysts would have two main advantages: they need only a mild pretreatment that involves low operating costs and they enable a higher throughput of product per unit catalyst mass.

The existence of W species on the surface of PdW and WPd catalysts less electron-deficient than on the monometallic WAl catalyst, suggest that some intermediate species are formed that produce a transfer of electrons from Pd to W. There is not a simple interpretation to explain the influence of the second metal on the Pd performance. Alkynes partial hydrogenation reactions are more or less sensitive to geometrical and electronic effects, being the latter the most important ones. The properties of palladium based bimetallic catalysts are related to the preparation method, which affects the electronic and chemical state of Pd and of the second metal, as well as their spacial distribution. As observed by XPS, the tungsten addition to the palladium catalyst reduced the electron deficiency of W. The lower reduction temperature employed, the lower electron deficiency of W. The modification of the electronic state of tungsten and palladium could be responsible for the better catalytic behavior, moreover considering the high electronic density of the alkyne triple bond. However, the influence of geometrical effects and/or mixed sites on the activity or selectivity of bimetallic catalysts cannot be discarded. More work is necessary to continue elucidating the selectivities and activities enhancement. If we compare bimetallic WPd and PdW catalysts reduced at 393 K, both present similar high values of selectivity but different total conversion values. The WPd_393 was much more active than the other. The characterization by XPS indicated that W had the same binding energy in both catalysts and therefore the difference in catalytic behavior could only be attributed to geometrical effects due to the possible decoration of Pd particles by WO_x species.

The prepared bimetallic catalysts were much more active than the Pd monometallic catalyst. Similar results were reported by L'Argentière and Fígoli [30] during selective hydrogenation of styrene. According to their report the bimetallic Pd-W/Al_2O_3 catalyst was more active than Pd/Al_2O_3.

In the case of the catalysts of the WPd series they have Pd metal particles reduced to a 52%. Their pattern of decreasing activity correlates with the increase in the temperature of reduction, the increase in the electron-deficiency of W, and the increase of the metal hydrogen chemisorption (as shown in Fig. 1A and Table 1). In this series the electronic effect is predominantly present.

The PdW series has a 57.8% of reduced Pd. For this series the values of selectivity and total conversion are very similar in spite of their different values of metal hydrogen chemisorption and W electrodeficiency. This seemingly contradiction was attributed to the presence of an effect of decoration of Pd particles by reduced W species. This decoration would produce the blocking of the Pd sites of high activity and selectivity for semihydrogenation. In this series the geometric factor is more important than the electronic effect.

4. Conclusions

Supported monometallic W and Pd catalysts and supported bimetallic PdW and WPd catalysts were prepared by incipient wetness impregnation of gamma alumina with a small load of these metals (2.4% W and 0.4% Pd).

The XRD, XPS, TPR and hydrogen chemisorption results reveals three important features in the case of the bimetallic catalysts: (a) surface amorphous WO_x are present; (b) surface W species are less electron-deficient than monometallic tungsten and could be formed by an electronic transfer from Pd to W (in total accordance with their electronegativities) or to the formation of a metallic bond between both metals; this effect is enhanced with a decrease in the reduction temperature and was remarkable at 393 K; (c) the hydrogen chemisorption of the Pd metal particles is increased at higher reduction temperatures in the WPd series but this effect is reversed in the case of the PdW series. The decrease in hydrogen chemisorption at higher reduction temperatures for PdW catalysts would be due to the decoration of Pd particles by W species.

The results of the catalytic tests show that the tungsten monometallic catalyst (WAl) is an active but low less selective catalytic system for the partial hydrogenation of hept-1-yne. The addition of a second metal to PdAl or WAl in order to form PdW or WPd catalysts greatly improves the activity for the conversion of hept-1-yne.

All the bimetallic catalysts had higher activity and similar or higher selectivity than the commercial Lindlar catalyst tested at the same reaction conditions.

The catalyst with the lowest electron-deficiency for the W atom, the WPd catalyst reduced at 393 K, was also the most active and selective catalyst for partial hydrogenation. The high activity and selectivity of the WPd catalyst series could be related to the interaction between the d and f electron orbitals of Pd and W. This interaction would favor the formation of a Pd-WO_x/Al_2O_3 highly active interface with highly exposed Pd atoms.

The bimetallic prepared presents also the advantages of low Pd loading and low cost of the tungsten precursor, that provides a cheaper catalyst with high activity and selectivity toward the production of the desired product.

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