

Stereoselective hydrogenation of phenyl alkyl acetylenes on pillared clays supported palladium catalysts

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Abstract

The stereospecific hydrogenation of phenyl alkyl acetylenes at 298 K and atmospheric pressure of hydrogen over Pd supported catalysts has been studied. The catalysts were prepared by impregnation Al-PILC and Ca-Mont with Pd(acac)₂ precursor, with metal content close to 1 wt.%. All the solids were characterised by nitrogen adsorption–desorption isotherms at 77 K, TPR, H₂ and CO chemisorption, XRD and TEM measurements. The reactions were found to be zero order concerning the alkyne concentration. At conversion levels up to 80% (reaction time lower than 90 min), only a limited overhydrogenation occurred. It was found that at higher reactant molecule: Pd atom ratios (R:P = 7000), the activity is approximately half of that obtained at lower R:P (R:P = 3500). The results suggested that the hydrogenation of phenyl alkyl acetylenes to *cis*-alkene is “structure insensitive”. All catalysts displayed high selectivity to *cis*-alkene isomer being the 1% Pd/Al-PILC the most active catalyst.

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1. Introduction

The catalytic hydrogenation of acetylenes is the most facile of all hydrogenation reactions, generally taking place in the presence of all other functional groups including conjugated dienes and aromatic groups. The complete hydrogenation of alkynes to alkenes (see Fig. 1) occurs over all common hydrogenation catalysts at room temperature and atmospheric pressure. This reaction and the related semihydrogenation to form alkenes is important in synthetic procedures because the acetylenic group can participate in a wide range of substitution reactions and, thus, can join two pieces of a carbon chain to produce a variety of aliphatic species.

Palladium (Pd) is the most selective of the noble metal catalysts for alkyne semihydrogenation with respect to over-

all alkene formation and the production of the *cis*-alkene. Pd is normally used as a supported heterogeneous catalyst and frequently in the presence of some additives to promote selectivity. Catalytic performance in heterogeneous systems is strongly influenced by, first, the ability to get reactants to the active sites, then to establish the optimum hydrogen:hydrocarbon surface coverage, and, finally, the rapid removal of the hydrogenated products. In the respect, the nature of the support (inertness, surface area, pore size distribution) controls the molecular access to the active sites and can also participate in unwanted side reactions through the so-called “spillover” effect [1].

A commonly used catalyst for the semihydrogenation of alkynes is a commercial Lindlar catalyst, calcium carbonate-supported palladium, modified by the addition of lead and, often, quinoline to improve selectivity [2]. Some works have indicated that the lead ions in the Lindlar catalysts block the more active hydrogenation sites on the palladium, thus inhibiting the alkene hydrogenation [3]. The use of secondary

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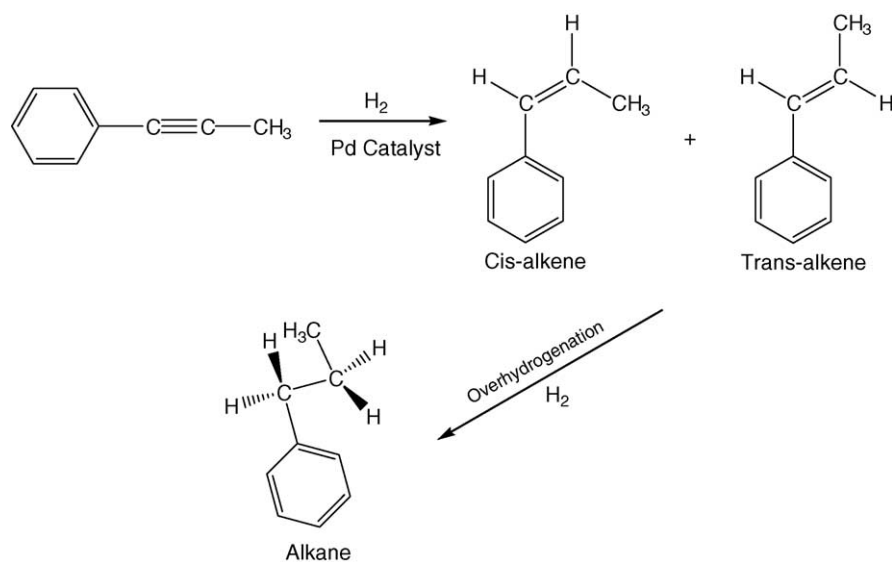


Fig. 1. Scheme of reaction for the stereospecific hydrogenation of 1-phenyl-1-propyne.

modifiers, such as quinoline, and the choice of an appropriate solvent, can also play important roles in directing semihydrogenation selectivity. Some zeolites have been successfully employed as supports for palladium catalysts [4]. In case of A zeolite, the limited accessibility of the pores structure of the solid decreased the activity and implies that only the extraframework Pd sites are catalysing the reaction of alkynes semihydrogenation.

The preparation and catalytic application of new materials such as: pillared clays, clay intercalated metal complex, M41S family, MSU-H initiated by Pinnavaia and coworkers [5–11], has attracted considerable attention [12–16]. These materials opened new opportunities to analyse the performance of Pd catalysts, as that usually involved in the production of fine chemicals. Mastalir and coworkers [17–19], prepared Pd intercalated in pillared clays catalyst via a novel synthetic method that provided finely distributed Pd particles placed mostly on the external surface of the clay lamellar, where the surfactant C₁₄TAB had a key role in the preparation of catalyst. The performance of Pd-pillared clay catalyst for the hydrogenation on different phenyl acetylenes, which allows a high selectivity to the *cis*-alkene was studied. The authors reported high *cis*-isomer stereoselectivity and a limited overhydrogenation on Pd catalysts having Pd content lower than 0.4%, behaviour attributed to the porosity of the support.

The aim of the present work has been to study the influence of the support, on the activity and selectivity in the stereospecific hydrogenation in liquid phase of various phenyl alkyl acetylenes. A montmorillonite, and aluminium pillared clay (synthesized in laboratory) have been used as supports of the Pd catalysts. The hydrogenations in liquid phase of the phenyl alkyl acetylenes (1-phenyl-1-propyne, 1-phenyl-1-butyne and 1-phenyl-1-pentyne) were performed at 298 K and 1 bar using THF (dried) as solvent. As comparison, the

commercial Lindlar catalyst (5% Pd/CaCO₃ poisoned with lead) was also studied.

2. Experimental

2.1. Materials

1-Phenyl-1-propyne, 1-phenyl-1-butyne and 1-phenyl-1-pentyne were commercially available (an Aldrich product of 99% purity) and used without further purification. Hydrogen (99.995% purity), an AGA product, was used as received. The solvent tetrahydrofuran (THF) was dried and distilled under nitrogen atmosphere. As comparison, the commercial Lindlar catalyst (5% Pd/CaCO₃ poisoned with Pb, an Aldrich product) was used.

2.2. Synthesis of catalysts

Two different supports were used: a commercial Ca-montmorillonite with a particle size <2 μm and a Al-PILCS obtained from a pillaring processes [20]. This later solid was prepared using as a starting material a chilean clay provided by Enacar Manto Tres-Claro (EM3C). It consists essentially of a mixture of illite, rucelite and caolinite. The illite is highly expansible giving to approximately 90% of smectite layers. In order to eliminate the carbonaceous species of the starting materials, the solid was treated with H₂O₂ (30%) repeatedly. Then the clay was ground and sieved to 200 mesh. Later on, it was exchanged with a 1 M aqueous solution of NaCl at 25 °C during 3 h under continuous stirring. Then, it was washed with distilled water up to no chlorine ions were detected. The particles smaller of 2 μm were separated by centrifugation and the remaining part of the solids were dried at 80 °C for 48 h. A 60% of yield referred to the clay

appropriate for PILCS preparation was obtained. The pillaring cation, $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ was obtained by a slow addition of 0.5N aqueous solution of NaOH to a 0.2N solution of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ using a OH/Al^{3+} equivalent ratio of 2 at 50 °C and 2 h of aging. The catalysts were prepared by impregnation using a slight excess of toluene solution of $\text{Pd}(\text{acac})_2$ required to fill the pore volume of the supports, in the required amount to get 1 wt.% of Pd. The solids were dried at 373 K and calcined at 673 K under air flow for 4 h. The solids were labelled as Pd/Ca-Mont and Pd/Al-PILC. Both solids were reduced in situ in hydrogen at 573 K for 1 h before their characterisation or catalytic evaluation.

2.3. Characterisation

The Pd contents of the catalysts were evaluated by molecular absorption at $\lambda = 462.5$ nm using a Shimadzu UV–vis spectrophotometer. Prior determination, the samples were dissolved in *aqua regia*. The palladium concentration was obtained by means of a calibration curve (slope = $5616 \text{ cm}^3/\text{mmol}$, $R^2 = 0.9997$).

X-ray diffraction (XRD) patterns were obtained on a Rigaku diffractometer using a Ni-filter and $\text{Cu K}\alpha_1$ radiation. Intensity was measured by scanning steps in the 2θ ranges first between 3° and 70° at 1° min^{-1} and then the region between 20° and 50° was rescanned at $0.25^\circ \text{ min}^{-1}$. The $d_{(001)}$ values were calculated from the first-order (0 0 1) Bragg reflections.

Nitrogen adsorption–desorption isotherms at 77 K, in the relative pressure range, 0.05–1.00 were carried out in an automatic Micromeritics ASAP 2010 apparatus, to determine the specific area and porosity of the solids. The specific area (S_g) was determined by means of the BET equation [21], whereas the micropore (V_0) was obtained by the Dubinin–Radushkevich equation [22]. The total pore volume (meso + micropore) was estimated from the N_2 adsorption isotherm by interpolating at $P/P^0 = 0.95$ according Gurtsovich rule and the volume of mesopores (V_m) was calculated by difference. The metal dispersion was determined by H_2 chemisorption at 343 K and CO adsorption at 298 K in the same equipment. Hydrogen chemisorption was carried out at 343 K in the pressure range 1–100 mmHg. Once the hydrogen isotherm was obtained, the sample was outgassed at the same temperature and a second hydrogen isotherm was carried out. The hydrogen uptake was evaluated from the irreversible adsorbed H_2 , as the difference between the first (total) and the second (reversible) isotherms in the pressure range 1–4 mmHg.

The metal particles-size distributions were obtained from transmission electron microscopy (TEM) micrographs, taken with a Jeol Model JEM-1200 EXII System. The samples were prepared by the extractive replica procedure.

2.4. Catalytic test

The hydrogenation in liquid-phase of the phenyl alkyl acetylenes compounds (1-phenyl-1-propyne, 1-phenyl-1-butyne and 1-phenyl-1-pentyne) was carried out in a batch

reactor at 298 K and 1 bar, using 25 mg catalyst. The reactants phenyl alkyl acetylenes were used as received. The solvent THF was freshly distilled before application. For each measurement, 25 mg of the catalyst was placed in the reaction reactor. Hydrogenation was conducted under efficient stirring (1400 rpm) to eliminate diffusion control. The total volume used was 15 ml. Different phenyl alkyl acetylene: Pd molar ratios (R:P) were used. Prior to reaction, the sample was reduced at 573 K during 1 h in H_2 flow and cooled to the reaction temperature. Then, the solution of phenyl alkyl acetylenes in THF was fed to the reactor under constant stirring. Samples were taken at different reaction times and analysed by a Star VARIAN 3400-CX gas chromatograph equipped with a DB-Wax (0.53 mm; 30 m) capillary column and a flame ionization detector (FID). The reactant: Pd ratios (R:P) were expressed as mole phenyl alkyl acetylene: mole Pd. The catalytic activities were characterized by the turnover frequencies (TOFs) and turnover numbers (TONs), determined from H_2 chemisorptions results.

3. Results and discussion

The XRD patterns (see Fig. 2) of the starting clay and Al-PILC exhibit three main X-ray peaks around 5–7°, 20° and 35° 2θ regions. The first peak is commonly assigned to the basal (0 0 1) reflection (see Table 1), while the second and third peaks are attributed to the two-dimensional (hk) planes. The Al-PILC support displays the (0 0 1) peak with high intensity even after pillaring. The basal spacing of starting clay, 12 Å, agrees with that usually reported for montmorillonite clays in the interlayer space. The solid intercalated with Al_{13} -Keggin polycation shows basal spacing of 18 Å. The high intensity observed for the basal reflection of Al-PILC indicates an expansion of the layer structure. The XRD patterns were recorded for all Pd catalysts. No significant differences compared to the starting supports were observed. No peaks due to Pd were detected, probably due to the low metal content or high metal dispersion and also no further structural

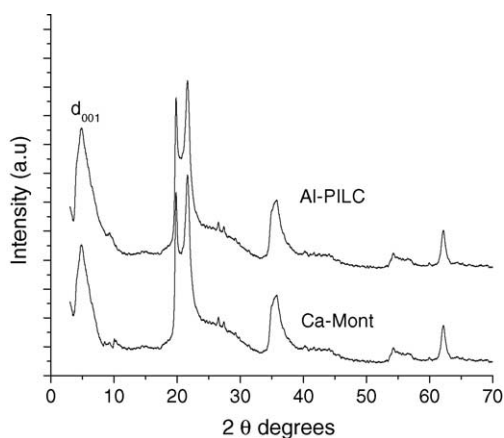


Fig. 2. XRD patterns of Al-PILC and Ca-Mont solids.

Table 1
Textural properties obtained from N₂ physisorption data and basal reflection of supports and catalysts

Sample	V ₀ (cm ³ /g)	V _m (cm ³ /g)	V _p (cm ³ /g)	S _g (m ² /g)	d ₀₀₁ (Å)
Ca-Mont	0.04	0.10	0.14	74	12
1% Pd/Ca-Mont	0.03	0.07	0.10	74	12
Al-PILC	0.09	0.07	0.16	196	18
1% Pd/Al-PILC	0.07	0.08	0.15	154	17

alterations in the supports were observed. The basal spacing was 17 and 12 Å for Pd/Al-PILC and Pd/Ca-Mont catalysts, respectively.

The variety of physical and structural characteristics of PILC may offer the commercial application of PILC to catalytic processes. The nitrogen adsorption–desorption isotherms at 77 K of the starting clay and pillared sample were examined. The clay and pillared sample used in the present study contains low microporosity. After pillaring the solids Type IV adsorption isotherms observed for the solids containing micropores and mesoporous according to Brunauer, Deming, Deming and Teller (BDDT) classification [21], due to the mesopores formed in the pore structure. The textural properties for supports are given in Table 1. As expected, the intercalation with Al₁₃-Keggin polycation caused a notable increase of both the specific surface area and the total and microporous volumes with respect to the starting clay. This agrees with the XRD pattern with respect to the aluminum pillar. The effect of incorporation Pd particles by impregnation with Pd(acac)₂ solution on specific surface area was also examined by the alteration of N₂ isotherm as shown in Fig. 3. Fig. 3 clearly reveals the addition of Pd significantly enhances the structural tolerance of the clays.

TEM micrograph of the 1% Pd/Al-PILC and 1% Pd/Ca-Mont showed a wide size distribution for the palladium crystallites formed, most of the palladium particles in the range 2–4 nm and small presence of agglomerate particles were observed for both catalyst. The observation of a nonspherical form for the palladium particles suggests that the particle morphology is strongly influenced by the presence of the

layered clay structure. Additionally, the possibility that the palladium particles may be stabilised with respect to a more spherical morphology as a consequence of interactions with the clay surface, cannot be neglected.

The metal particle size values obtained by hydrogen chemisorption and TEM for 1% Pd/Ca-Mont and 1% Pd/Al-PILC catalyst were in good agreement. The higher metal particle size obtained from TEM may be attributed to the evaluation of a lower proportion of the smallest Pd particles. A summary of these results is given in Table 2. The H₂ chemisorption (total and reversible isotherms) and CO chemisorption results are also showed in Table 2. The observed differences between H/Pd and CO/Pd ratios may be explained taking into account the difficulty to determine a precise stoichiometry for the adsorption of CO on Pd particles. Metal particle sizes evaluated from hydrogen chemisorption data revealed that both catalysts possesses different values. H₂ and CO uptake of Lindlar catalysts showed lower values compared with the other studied catalysts revealing a lower extent of surface palladium. Two main effects may explain the decrease in the H/Pd ratio in the Lindlar catalysts: (i) the surface coverage of Pd by PbO; (ii) ensembles of Pd are destroyed by the insertion of Pb⁰ in the crystallites, thus, leading to a significant decrease in the ability to chemisorbs hydrogen.

Mass transfer can play an important role in liquid phase hydrogenation using porous catalysts. Therefore, it is critically important that mass transfer effects are ruled out before attempting to obtain reliable kinetic data. In order to minimize mass transfer limitations the smallest catalyst particle sizes (<200 μm) and highest stirring speed were used (1400 ppm). These two precautions served to increase the rate of mass transfer from the gas to the liquid phase, to increase the rate of reactant transfer from the bulk liquid to the catalyst surface, and to minimise internal diffusion resistance. To check that mass transfer was not rate controlling the conversion of phenyl alkyl acetylene, the reaction was studied under standardized conditions over a range of different catalyst masses. The absence of mass transfer limitations was confirmed by a straight-line plot of conversion against catalyst mass (Fig. 4).

The stereospecific hydrogenation of phenyl alkyl acetylenes has been investigated on various supported Pd catalysts [13,17–19,23–25]. For Pd/carbon catalyst, high selectivity to the alkene is maintained up to conversions of 85% for the phenyl acetylene [26]. For PdZr and PdCuZr prepared from amorphous precursors, a ~98% alkenes selectivity for hydrogenation of isomeric pentynes and a linear trend for percentage of conversion versus time have been reported [27].

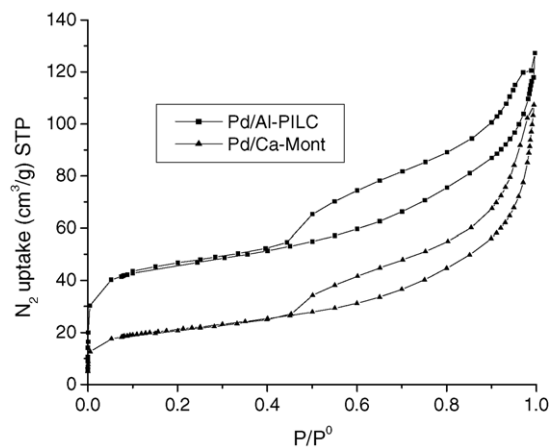


Fig. 3. Nitrogen isotherms of 1% Pd/Al-PILC and 1% Pd/Ca-Mont catalysts after impregnation with Pd(acac)₂.

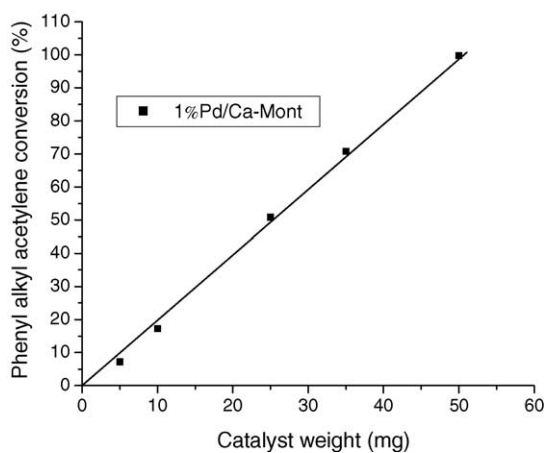


Fig. 4. Phenyl alkyl acetylene conversion as a function of catalyst mass. Catalyst = 1% Pd/Ca-Mont, $T = 25\text{ }^{\circ}\text{C}$, $P_{\text{H}_2} = 1\text{ atm}$, time of reaction = 30 min.

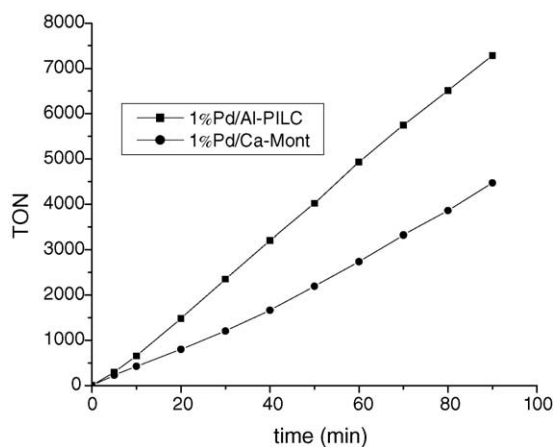


Fig. 5. Evolution of turnover number with time for supported Pd catalysts: 1-phenyl-1-butyne hydrogenation at 298 K, 1 bar H_2 pressure and R:P = 3500.

Michalska et al. [28] reported for hydrogenation of 1-phenyl-1-propyne and 1-phenyl-1-butyne, a 77 and 80% *cis*-alkene selectivity, respectively, over palladium catalysts supported on heterocyclic polyamides.

The hydrogenation of phenyl alkyl acetylenes was carried out at 298 K and 1 bar in THF during 120 min, at different R:P ratios. No catalyst deactivation during the catalytic run was observed. Fig. 5 displayed the evolution of TON on reaction time for 1-phenyl-1-butyne hydrogenation on a representative catalyst. The TON plots showed at the beginning very similar values for both catalysts, however at higher time a noticeable difference in the activity of the catalysts is observed. This behavior can be explained due to pillared

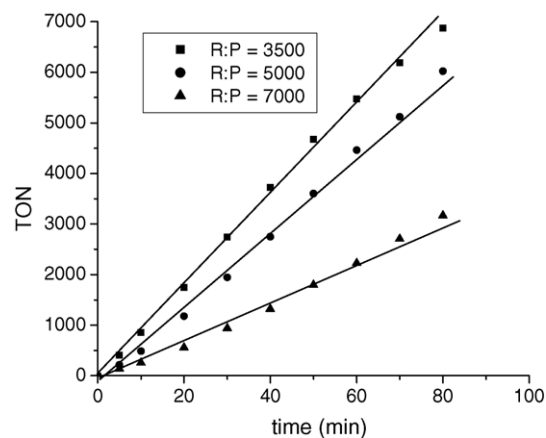


Fig. 6. Turnover number vs. reaction time for different R:P molar ratios: 1-phenyl-1-butyne hydrogenation at 298 K, 1 bar H_2 pressure, catalyst: 1% Pd/Al-PILC.

process causing an increase in the specific area, total pore volume and micropores volume, with respect to the Ca-Mont support favoring the displacement of reactants and products through the laminar structure of the support. This trend was observed for all studied systems. Nevertheless, the activity in the reaction mentioned previously on the 1% Pd/Ca-Mont catalyst was slower compared to that of 1% Pd/Al-PILC catalyst, which is consistent with values of H/Pd ratio obtained by H_2 chemisorption (Table 2). The differences observed in H/Pd ratios indicates a decreased in the number of active sites in the catalyst, which is related to the presence of larger particles in the 1% Pd/Al-PILC catalyst and can be explained for the creation of stronger sites of anchorage Al–OH type.

On the other hand, at higher R:P ratios the activity is approximately two times lower than that exhibited by the Pd supported catalysts at lower R:P ratios. This trends is in agreement with the results reported by Mastalir et al., for low-loaded Pd-montmorillonite catalysts. It was found that the conversion decreases as the mole reactant:mole Pd ratio increases [18]. The drop in the TON observed as R:P increases from 3500 to 7000 was rather significant (Fig. 6). For this reason we decided that further measurements should be conducted at R:P = 3500, where the TON of the reactant was still reasonably high (TON = 6900). It is worth while mentioning that the R:P ratios used in our experiments were substantially higher than those used for the hydrogenations of different alkyne derivatives on Pd-montmorillonites prepared by other methods [23], which confirms the outstanding activities of our Pd supported catalysts. In the hydrogenation of 1-phenyl-1-butyne, at R:P molar ratios of 5000 and 7500 the

Table 2

Pd loading, H/Pd and CO/Pd ratios and metal particle size evaluated by H_2 and CO chemisorption and TEM of Pd supported catalysts

Catalyst	Pd (%)	H/Pd	CO/Pd	d_{H_2} (nm)	d_{CO} (nm)	d_{TEM} (nm)
1% Pd/Ca-Mont	0.97 ^a	0.30	0.12	3.4	8.4	4.0
1% Pd/Al-PILC	0.98 ^a	0.48	0.21	2.0	3.7	2.7
Lindlar catalyst	5	0.02	0.01	–	–	–

^a Determined by molecular absorption.

Table 3
The stereospecific hydrogenation of 1-phenyl-1-propyne at 298 K on different catalysts at R:P = 3500

Catalysts	TOF ^a (s ⁻¹)	<i>k</i> (×10 ³ mol min ⁻¹ g ⁻¹)	<i>S</i> _{cis} (%)	<i>S</i> _{trans} (%)	<i>S</i> _{cis} /(<i>S</i> _{cis} + <i>S</i> _{trans})
1% Pd/Ca-Mont	0.14	4	78	3	0.97
1% Pd/Al-PILC	0.37	13	90	3	0.96
Lindlar ^b	0.07	0.1	96	2	0.98

^a 20% conversion.

^b R:P = 250.

TON levels decreased at 1900 and 850, respectively, at 30 min on stream. These results at R:P = 5000 are in agreement with previous reported for 1% Pd/MCM-41 catalyst in the hydrogenation of phenyl alkyl acetylenes [29]. Eventhough the trends were similar for all the studied systems, significant differences in the catalytic activity were observed, being the 1% Pd/Al-PILC catalyst, the most active.

The effect of Pd dispersion on the hydrogenation of 1-butyne has been widely studied and it is well known that changes in the metal dispersion, i.e. different particle sizes, lead also to changes in TOF and selectivity. Several authors [30–35] have reported a decrease in the specific activity as metal particle size decreases, whereas others found that the TOF increases upon increasing the metal dispersion [36]. Moreover, recent publications have pointed out that this type of reactions are structure sensitive or only small changes in activity occurs, but most of the studies agree with a drop in the activity with an increase in the metal dispersion. The selectivity of these Pd supported catalysts was compared with that exhibited by the Lindlar catalyst, which is still regarded as the most efficient catalyst in the hydrogenation of alkynes [2]. These results are compiled in Table 3 for 1-phenyl-1-propyne hydrogenation. It can be seen that the TOF exhibited for 1% Pd/Al-PILC catalyst was slightly higher compared to that of 1% Pd/Ca-Mont and the commercial Lindlar catalyst. The presence of Pb in the Lindlar catalyst can produce a decreased in the TOF values respect at 1% Pd/Al-PILC catalyst, indicative of an electronic effect from lead to palladium or a surface coverage of palladium by lead species. This effect is observed for phenyl alkyl acetylenes hydrogenation over palladium supported in solid mesoporous catalysts poisoned with lead [29]. However, the amount of Pd required for similar catalytic performance was considerably lower than that of the Lindlar catalyst and the R:P ratio used for the performance with commercial Lindlar catalyst was much lower because at high R:P ratio the conversion levels is lower than 1%.

The selectivity to the *cis*-isomer compared at the same conversion level, clearly indicates that the commercial Lindlar catalyst was the most efficient catalyst (*S*_{cis} = 96%) at R:P = 250. Nevertheless, the *cis*-selectivity obtained for the 1% Pd/Al-PILC and 1% Pd/Ca-Mont is reasonably acceptable, predominating the 1% Pd/Al-PILC catalyst and the *S*_{cis}/(*S*_{cis} + *S*_{trans}) ratio for the three catalysts were practically identical (see Table 3). The main hydrogenation product for all the studied systems was the *cis*-isomer. Fig. 7 displays the evolution of the selectivity with conversion level in the

1-phenyl-1-butyne hydrogenation for a representative catalyst, indicating a predominant formation of the *cis*-isomer. It is generally accepted that the *cis* product is formed by addition of two adsorbed hydrogen from below axis of the triple bond [37,38]. For the hydrogenation of 1-phenyl-1-butyne on Pd/Al-PILC, a conversion of 100% was obtained at 110 min of reaction at R:P = 3500. The initial selectivity obtained at 5% conversion for *cis*-1-phenyl-1-butene formation was 83% and decreased to 62% at 99% of conversion. Fig. 7 reveals that the overhydrogenation product 1-phenyl-1-butane was formed via simultaneous hydrogenation of the *cis*-1-phenyl-1-butene molecule at high conversions [37]. The trend was similar for all the studied systems. The mode of adsorption is the only defining factor in the alkyne reactivity. Alkynes are known to have strong complexing abilities and this is one of the reasons for the high semihydrogenation selectivity over Pd, the adsorbing alkyne prevents the readsorption of the product alkene and hence the consecutive hydrogen addition cannot take place [39–41].

The TON plot obtained for Pd catalysts (Fig. 5) exhibited a linear trend up to a reaction time of 100 min (corresponding to a TON = 7200), which confirmed that zero order kinetics applies, i.e. the initial rate of phenyl alkyl acetylene hydrogenation corresponds to the reaction rate. Similar observations were made for all catalysts studied. The results of the comparative investigation of the Pd catalysts are collected in Table 4. The turnover frequencies (TOF) and specific rate constant (*k*), are practically constant at different R:P ratios,

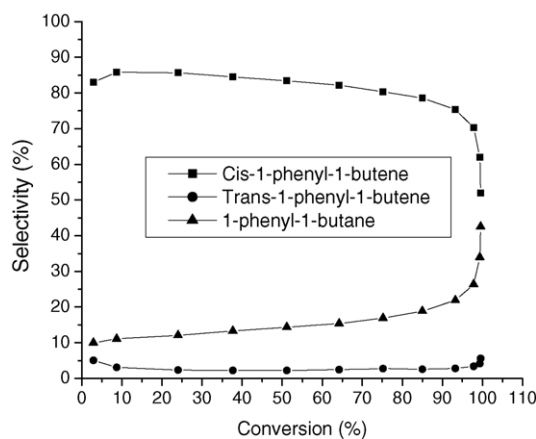


Fig. 7. Selectivity to hydrogenated products in the hydrogenation of 1-phenyl-1-butyne over 1% Pd/Al-PILC catalyst at 298 K, 1 bar H₂ pressure and R:P = 3500.

Table 4

Specific rate constant (k) and turnover frequency in the hydrogenation of phenyl alkyl acetylenes at 298 K at different R:P ratios on 1% Pd/Al-PILC catalyst

R:P ratio	k ($\times 10^3$ mol min $^{-1}$ g $^{-1}$)			TOF ^a ($\times 10^3$ s $^{-1}$)		
	C ₉ H ₈	C ₁₀ H ₁₀	C ₁₁ H ₁₂	C ₉ H ₈	C ₁₀ H ₁₀	C ₁₁ H ₁₂
3500	0.36	0.40	0.33	13	15	11
5000	0.32	0.34	0.35	11	12	12
7000	0.21	0.20	0.27	4	5	7

C₉H₈: 1-phenyl-1-propyne; C₁₀H₁₀: 1-phenyl-1-butyne; C₁₁H₁₂: 1-phenyl-1-pentyne.

^a Conversion level 20%.

with the differences falling within experimental error. Moreover, the structure insensitivity [42], for the whole range of metal dispersion considered ($30\% \leq D_x \leq 48\%$), is unusual in the hydrogenation of alkynes. It is well known [43] that the TOF for semihydrogenation of alkadienes [43,44] with supported Pd catalyst is at least 20 times higher than the TOF for the semihydrogenation of alkynes [43,45]; this experimental result cannot be explained exclusively by the difference in bond strength of the two adsorbed species to palladium. Previous studies reported in the literature suggested that alkyne hydrogenation is a structure sensitive reaction at medium to high dispersions [30,45]. Although the TOF values in Table 4 did not confirm structure sensitive for the phenyl alkyl acetylenes hydrogenation, a crystallite size effect may be suggested in terms of the conversions. The work of Mastalir and Király [17], using Pd-hydrotalcites affirm that a molecular sieving effect may be excluded and mole reactant:mole Pd play an important role in the alkynes hydrogenation. This affirmation is because for the presence of Pd particles on the external surface of the hydrotalcite host. Crocker et al. [46], reports the critical dimension of phenyl acetylene, essentially determined by the thickness of the benzene ring, is 3 Å. It is therefore suggested that the apparent substrate size dependence arises from spatial requirements for reactant chemisorption both on the external surface sites and in the restricted interlamellar region. Several studies have demonstrated the shape selectivity properties of hydrogenation catalysts based on clays intercalated with metal particles and metal complexes [47–49]. Pinnavaia [5], has pointed out that as a consequence of this effect, efficient catalytic discrimination among substrates on the basis of size or shape can be expected only when the differences in the critical dimensions are larger than the spread in interlayer spacing.

On the other hand, a comparison of the selected data in selectivity to the *cis*-isomers at different R:P ratios is reported in Table 5. The selectivity to the *cis*-isomer is rather constant up to approximately 80% of conversion and then decreases. Simultaneously, and increase in both, the *trans*-isomers and the saturated compound derivative is observed. As reported in the literature, *trans*-isomer is always formed in the hydrogenation of alkynes, either as initial products or as a result of isomerization of the *cis*-isomers [28,50]. According to the previous data reported for substituted alkynes, hydrogenation

Table 5

Selectivity to the *cis*-isomer in the hydrogenation of phenyl alkyl acetylenes at 298 K at different R:P ratios on 1% Pd/Al-PILC catalyst

R:P ratio	Selectivity to <i>cis</i> -isomer ^a (%)			Selectivity to <i>cis</i> -isomer ^b (%)		
	C ₉ H ₈	C ₁₀ H ₁₀	C ₁₁ H ₁₂	C ₉ H ₈	C ₁₀ H ₁₀	C ₁₁ H ₁₂
3500	89	86	83	89	84	81
5000	88	88	75	90	88	73
7000	90	91	83	92	92	84

C₉H₈: 1-phenyl-1-propyne; C₁₀H₁₀: 1-phenyl-1-butyne; C₁₁H₁₂: 1-phenyl-1-pentyne.

^a Conversion level 10%.

^b Conversion level 40%.

tion of the *cis*-alkene is likely to take place via desorption and a subsequent readsorption of the alkene molecules [37]. It is generally accepted that direct *trans*-isomers formation may occur via the addition of molecular hydrogenation to the adsorbed alkyne molecule [37].

4. Conclusions

In the present study, the effect of the support on the catalytic performance of palladium supported catalysts were investigated. The Pd supported on pillared clays are effective catalysts in the stereospecific hydrogenation of phenyl alkyl acetylenes in the liquid phase. The catalytic performances for all samples studied were different. A 1% Pd/Al-PILC catalyst was more active and most stereoselective than 1% Pd/Ca-Mont catalyst due to the expansion of the layer structure. The catalytic activity decreases with increased the R:P molar ratios due to preferential adsorption of alkynes molecules. The hydrogenation of phenyl alkyl acetylenes to *cis*-alkene may be regarded as “structure insensitive reaction”.

The main hydrogenation product was the *cis*-alkene; only at high conversion levels of the overhydrogenated appear. For all reactions, *cis*-alkene stereoselectivities of at least >80% for all R:P molar ratios studied were obtained. The amount of Pd required for similar catalytic performance was considerably lower than that of the commercial Lindlar catalyst.

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