Alkynes hydrogenation over Pd-supported catalysts

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The liquid-phase stereoselective hydrogenation of phenyl alkyl acetylenics at 298 K and atmospheric pressure on Pd-supported catalysts has been studied. The catalysts were prepared by impregnation of $Pd(acac)_2$ precursor (1 wt% of Pd) on different siliceous substrates such as amorphous SiO_2, mesoporous MCM-41 and silylated MCM-41. The poisoning effect of lead incorporation on the supported palladium was also studied. All the catalysts displayed high selectivity to *cis*-alkene isomer, with Pd/MCM-41 being the most active catalyst. Deliberately adding lead to the base, palladium catalysts underwent changes in the selectivity to *cis*-alkene isomer and a significant drop in the activity. All the solids were characterized by nitrogen adsorption–desorption isotherms at 77 K, TGA, TPR, H_2 and CO chemisorption, XRD, XPS, and TEM.

KEY WORDS: palladium; MCM-41; phenyl alkyl acetylenics; hydrogenation; stereoselectivity.

1. Introduction

The selective half hydrogenation of alkynes is a particularly important type of reaction in the context of fine chemical manufacture. The acetylenic group readily participates in substitution reactions enabling the formation of new carbon–carbon bonds and hydrogenation leading to alkene or alkane species, among others. The use of synthetic alkynes has been exploited in the synthesis of biologically active compounds, e.g., insect sex pheromones (pest control) and vitamins [1].

Palladium catalysts used for the selective hydrogenation of alkenes in industrial scale contains a low palladium loading (0.01–0.03% weight) in a highly dispersed state. The effect of metal dispersion, carbon deposits, and the use of promoters and additives on the catalytic performance during alkynes hydrogenation have also been reported [2–4]. Attempts have been made to relate the activity of palladium catalysts during the partial hydrogenation of superior alkynes with the nature and porosity of the support substrate. The use of the new materials of the M41S family opened new opportunities to analyze the performance of palladium catalysts. These materials appear specially interesting because their mesoporous may allow an easy access of the large molecules, as that usually involved in the production of fine chemicals, to the active sites. The preparation of this type of solids was initiated by Pinnavaia [5–6], and it has been widely developed by other authors [7–8]. Mastalir *et al.* [9] pointed out that the porosity of the support may significantly affect the performance of Pd/montmorillonite catalyst for the hydrogenation of 1-phenyl-1-pentyne, which allows a high selectivity to the *cis*-alkene. The high *cis*-isomer stereoselectivity and the limit of overhydrogenation at such low palladium contents is attributed to the porosity of the support.

This work was undertaken with the aim to study the influence of the support, and also the poisoning of the palladium sites with lead, on the activity and selectivity in the stereoselective hydrogenation in liquid phase of the phenyl alkyl acetylenics. A commercial silica, an MCM-41 type, and a silylated MCM-41 substrate have been used as supports of the palladium catalysts. Specific surface area was evaluated from the nitrogen adsorption isotherms, metal dispersion from H_2 and CO chemisorptions and TEM, structure by XRD (X-ray diffraction), and chemical species by XPS. The hydrogenation in liquid phase of the phenyl alkyl acetylenics (1-phenyl-1-propyne, 1-phenyl-1-butyne and 1-phenyl-1-pentyne) were performed at 298 K and 1 bar using THF as solvent.

2. Experimental

2.1. Preparation

Three different supports were used: a commercial SiO_2 (BASF D11-11), $S_{BET} = 85\,m^2/g$, $r_p = 80\,Å$, $V_p = 0.16\,cc/g$; a mesoporous material type MCM-41, $S_{BET} = 984\,m^2/g$, $r_p = 22\,Å$, $V_p = 0.89\,cc/g$; and a silylated MCM-41, $S_{BET} = 1016\,m^2/g$, $r_p = 24\,Å$, $V_p = 0.72\,cc/g$. The synthesis of MCM-41 was performed using a standard procedure [10]. The resulting synthetic gel of composition $SiO_2 : CTABr : TMAOH : H_2O = 1 : 0.15 : 0.26 : 24.3$. An aliquot of this solid was silylated using 1,1,1,3,3,3 hexamethyldisilazane (HMDS)

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as a silylating agent. A solution of HMDS: toluene $= 1 : 20$ was added to the calcined samples after vacuum. The mixture was refluxed for 2 h at 393 K with magnetic stirring under argon. The volatiles were stripped on a refrigerant and the dry powder was washed two or three times with toluene, dried and calcined as described above.

The catalysts were prepared by impregnation using a slight excess of solution required to fill the pore volume of the supports with a solution of $Pd(acac)_2$ in toluene, in the required amount to get 1 wt% of palladium. The solids were dried at 373 K and calcined at 673 K under airflow for 4 h. The solids were labeled as Pd/SiO_2, Pd/MCM-41, and Pd/MCM-41-Si. An aliquot of the previously prepared catalysts was poisoned by adsorption of a solution of $Pb(C_2H_3O_2)_2 \cdot 3H_2O$ in toluene, in the required amount to get 1 wt% of lead, followed by drying and calcination step at 373 and 673 K, respectively. Three new catalysts were obtained according to the previous procedure: Pb-Pd/SiO_2, Pb-Pd/MCM-41, and Pb-Pd/MCM-41Si. All catalysts were reduced *in situ* in hydrogen at 573 K for 1 h before their characterization or catalytic evaluation.

2.2. Characterization

Specific area and porosity were obtained with an automatic Micromeritics apparatus Model ASAP 2010 using nitrogen gas as adsorbate at the liquid nitrogen temperature in the 0.05–0.995 relative pressure range. The dispersion of the metal was determined by H_2 and CO chemisorption at 343 K in the same equipment. Hydrogen chemisorption was carried out at 298 K in the pressure range of 1 to 100 mm Hg. Once the hydrogen isotherm was obtained, the sample was outgassed at room temperature and a second hydrogen isotherm was determined at the same temperature. The hydrogen uptake was evaluated from the irreversible amount of adsorbed CO as difference between the first (total) and the second (reversible) isotherm within the pressure range of 1 to 4 mm Hg. Thermogravimetric analysis (TGA) of the supports was carried out in a Mettler Toledo TGA/SDTA851e apparatus in a temperature range of 273 to 873 K. TPR experiments were carried out in a TPR/TPD 2900 Micromeritic system provided with a thermal conductivity detector. The reducing gas was a mixture of 5% H_2/Ar ($40\,cm^3/min$) and a heating rate of 10 K/min was employed. X-ray diffraction patterns were obtained on a Rigaku diffractometer using a Ni-filter and Cu $K\alpha_1$ radiation. Intensity was measured by scanning steps in the 2θ range, first between 3 and 70° at 1°/min, and then the region between 20 and 50° was rescanned at 0.25°/min. TEM micrographs were obtained in a Jeol Model JEM-1200 EXII system. The samples were prepared by the extractive replica procedure.

Photoelectron spectra (XPS) were recorded using an Escalab 200R spectrometer provided with a hemispherical analyzer, operated in a constant pass energy mode and Mg $K\alpha$ X-ray radiation ($h\nu = 1253.6$ eV) operated at 10 mA and 12 kV. The system was provided with a reaction cell that allows pretreatment at high temperatures. The samples were pressed in a hydraulic die to form thin, smooth discs and placed in the cell. The catalysts were reduced *in situ* in hydrogen at 573 K for 1 h and then transported to the analysis chamber without contact with air. The surface Pd/Si, Pb/Si ratios were estimated from the integrated intensities of Pd $3d_{5/2}$, Pb $4f_{7/2}$, and Si 2p lines after background subtraction and corrected by the atomic sensitivity factors [11]. The line of Si 2p at 103.4 eV was used as an internal standard. Palladium and lead peaks were decomposed into several components assuming Gaussian–Lorentzian shapes.

2.3. Catalytic activity

The hydrogenation in liquid phase of the phenyl alkyl acetylenic compounds (1-phenyl-1-propyne, 1-phenyl-1-butyne, and 1-phenyl-1-pentyne) (ALDRICH 99% of purity) was carried out in a batch reactor at 298 K and 1 bar H_2 pressure using 25-mg catalyst. A phenyl-alkyl-acetylenics : Pd molar ratio of 5000 was used, similar to that employed for Mastalir *et al.* [12] for these kind of reactions. 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 solvent (dried THF) was injected and the phenyl-alkyl-acetylenics were fed under constant stirring. Samples were taken at different reaction times and analyzed by a gas chromatograph Star VARIAN 3400-CX provided with a capillary column DB-Wax (0.53 mm; 30 m) and flame ionization detector (FID).

3. Results and discussion

XRD analysis of the samples allowed to confirm that the mesoporous MCM-41 material was obtained. The peaks corresponding to (100), (110), (200), and (210) planes of a hexagonal structure with symmetry P6 for the reflection planes (hk0) were found. On the other hand, the values of the parameter "a_o" of the hexagonal pore arrangement for MCM-41 (noncalcined), MCM-41 (calcined), and MCM-41-Si substrates were 50, 46, and 47 Å respectively and were in good agreement with those previously reported by Beck *et al.* [10]. TG analysis of the MCM-41 support showed three weight-loss peaks associated with exothermic processes. The former between 298 and 403 K corresponds to the desorption of physisorbed water on the surface. The second and third steps, at 403–593 K and above 593 K, are mainly attributed to the decomposition and oxidation of the organic matter associated with condensation of silanol

Table 1
H/Pd and CO/Pd ratios obtained from chemisorption data and metal particle size of Pd-supported catalysts

Catalysts	H/Pd	CO/Pd	d_{H_2} (nm)	d_{CO} (nm)	d_{TEM} (nm)
Pd/SiO_2	0.14	0.14	6.7	6.7	4.0
Pd/MCM-41	0.21	0.13	4.5	7.2	3.2
Pd/MCM-41-Si	0.085	0.057	11	16	6.0
Pb-Pd/SiO_2	0.011	0.006	—	156	—
Pb-Pd/MCM-41	0.026	0.021	—	45	—
Pb-Pd/MCM-41-Si	0.010	0.009	—	104	—

groups respectively. TEM micrograph of the calcined MCM-41 materials showed typical shapes of these solids with a regular hexagonal array of mesoporous channels can be observed. With regard to the TEM of the catalytic materials, a very narrow palladium particle size distribution was observed on the SiO_2 and MCM-41 supports. Conversely, in the silylated samples, the distribution was more heterogeneous, showing small particles of comparable size to that observed in MCM-41 and silica, and also an important fraction of larger particles. A summary of these results is given in table 1. It also compiles the H/Pd and CO/Pd ratios obtained from chemisorption data. Both ratios are in reasonable agreement, and the observed differences may be explained by taking into account the difficulty in determining a precise stoichiometry for the adsorption of CO on palladium particles. The values of the metal particle size obtained by chemisorption and TEM showed similar values for the monometallic catalysts. However, a significant drop in the H/Pd ratio is observed for the catalysts poisoned by lead. This behavior may be attributed to the fact that lead is deposited on metallic sites of palladium, and, therefore, the lead ensembles are destroyed. Obviously, the evaluation of lead particle size for the binary Pb-Pd systems is meaningless.

Figure 1 shows the TPR profiles for catalysts used. Quantitative reduction of palladium oxides takes place at low temperatures (> 400 K). On the other hand, the reduction of palladium oxides shifts approximately at 30° higher and the reduction of PbO takes place at temperatures close to 700 K and higher temperatures. The interaction between palladium and lead is responsible for the observed shift. It should be emphasized that the reduction of palladium oxides occurs at approximately 100 K lower than PbO or PbO-supported samples. This behavior is explained considering that the reduction of PbO is catalyzed by reduced palladium, in which H_2 spillover plays an important role. The temperature of reduction for the catalysts supported in MCM-41 is slightly high owing to the strong interaction of the species that are confined inside the channels; this is verified with the Pd/MCM-41-Si sample (not shown) in which the peak of reduction of palladium appears at lower reduction temperatures.

Figure 2 displays the Pd $3d_{5/2}$ and Pb $4f_{7/2}$ core-level spectra of a representative Pb-Pd catalyst. The Pd 3d core-level spectra for the reduced Pd/MCM-41 and Pb-Pd/MCM-41 catalysts are shown in figures 2(a) and (b) respectively. A slight shift to higher binding energies in the Pb-Pd samples is observed, indicative of an electronic transfer from lead to palladium. Figure 2(c) shows the spectra of Pb 4f for the bimetallic Pb-Pd/MCM-41. The presence of both Pb^0 and Pb^{2+} are clearly seen. Metallic lead is formed by reduction of Pb^{2+}. This reduction process may be favored by the hydrogen spillover produced on Pd^0 surface. Table 2 compiles the binding energies of Pd $3d_{5/2}$ and Pb $4f_{7/2}$ core levels for

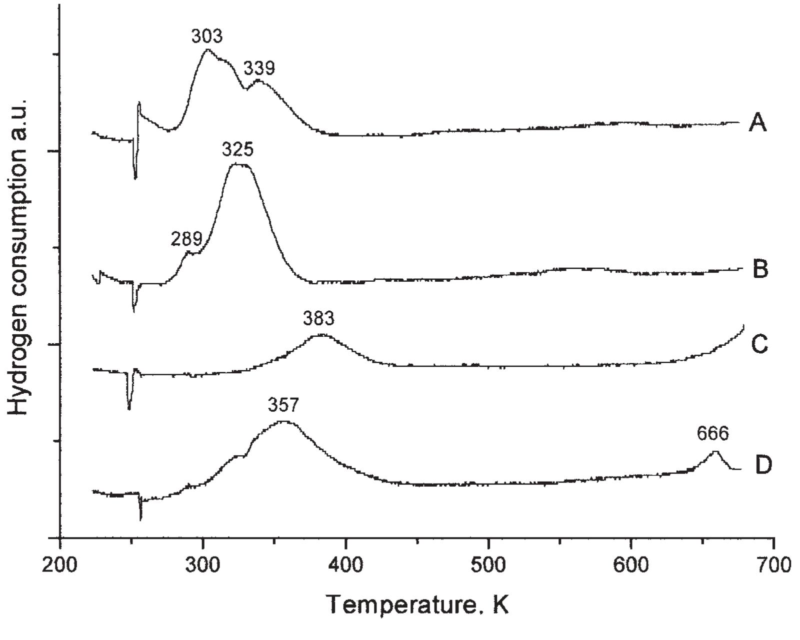

Figure 1. TPR profiles for different Pd-supported catalysts: (A) Pd/MCM-41, (B) Pd/SiO_2, (C) Pb-Pd/MCM-41 and (D) Pb-Pd/SiO_2.

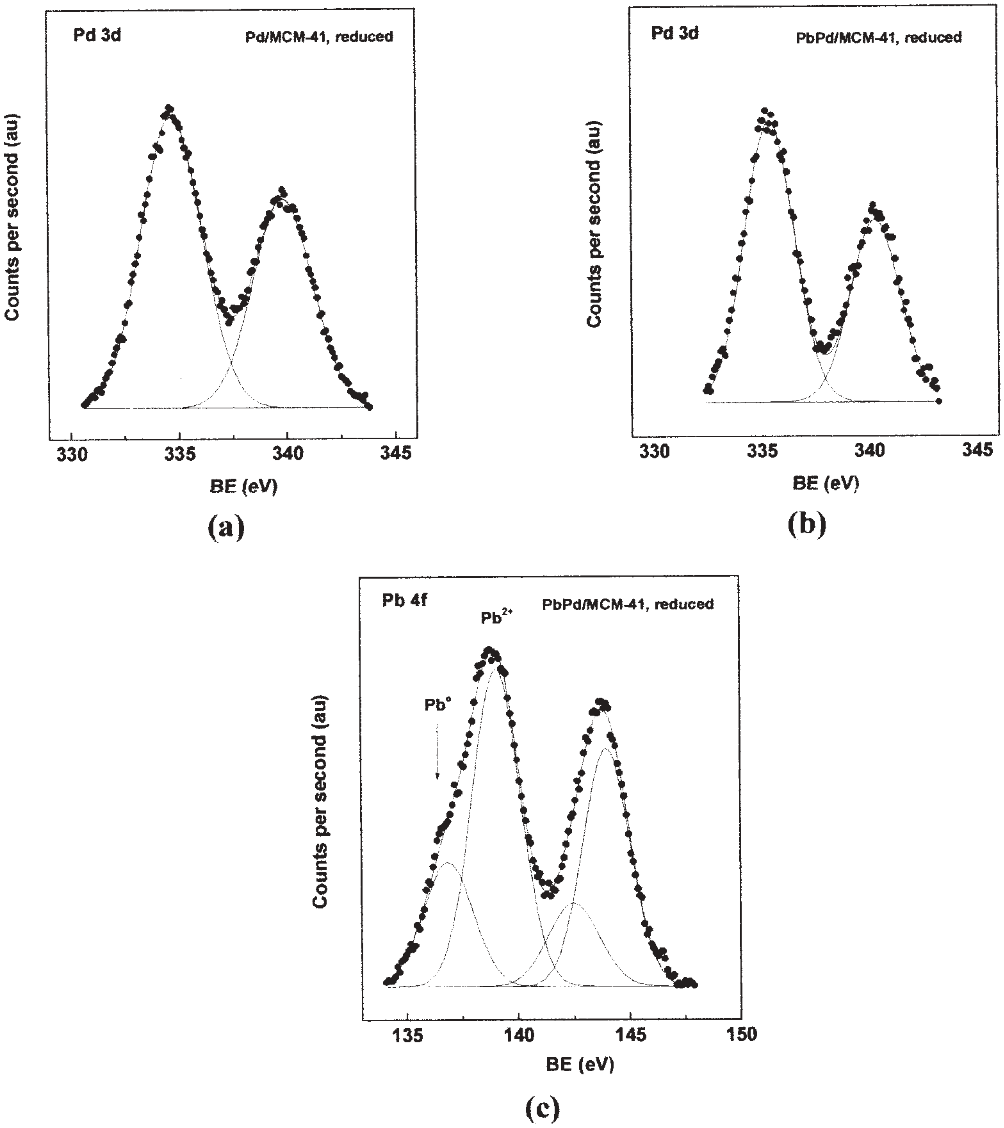

Figure 2. XP spectra of (a) Pd $3d_{5/2}$ of Pd/MCM-41, (b) Pd $3d_{5/2}$ of Pb-Pd/MCM-41, (c) Pb 4f of Pb-Pd/MCM-41 core levels of the reduced catalysts.

the studied catalysts and also the Pd/Si and Pb/Si surface atomic ratios. The Pd/Si ratios in the monometallic catalysts show comparable values, in agreement with the chemisorption results, indicating that both catalysts possess similar metal particle sizes. Additionally, lead incorporation produces a significant decrease in the Pd/Si ratio, indicative of a surface coverage of palladium by lead species. The fact that the decrease in the Pd/Si ratio from palladium catalysts to the lead-poisoned catalysts is smaller than the observed decreases in H/Pd ratio suggests that, apart from the surface coverage of palladium by PbO, ensembles of palladium

Table 2
Binding energies (eV) of core levels and surface atomic ratios of reduced Pd-supported catalysts

Catalyst	BE Pd $3d_{5/2}$	BE Pb $4f_{7/2}$	Pd/Si atom	Pb/Si atom
Pd/SiO_2	335.0	—	0.014	—
Pd/MCM-41	334.8	—	0.013	—
Pd/MCM-41-Si	—	—	—	—
Pb-Pd/SiO_2	335.4	136.9 (23) 139.0 (77)	0.007	0.004
Pb-Pd/MCM-41	335.4	136.9 (23) 139.0 (77)	0.004	0.027
Pb-Pd/MCM-41-Si	—	—	—	—

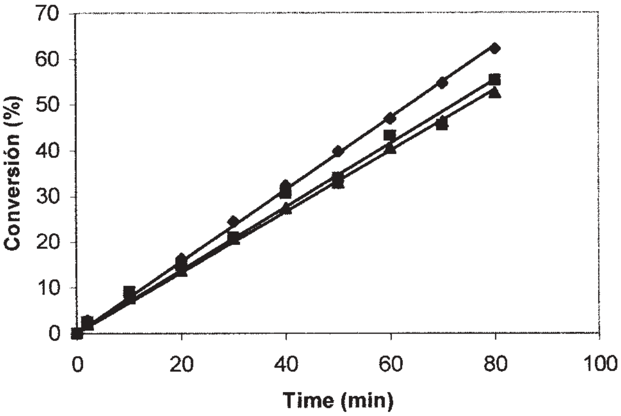

Figure 3. Evolution of conversion level on time for the Pd/MCM-41 catalyst. (◆), 1-phenyl-1-pentyne; (■), 1-phenyl-1-butyne; (▲), 1-phenyl-1-propyne.

are destroyed by the insertion of Pb^0 in the crystallites, thus resulting in a significant decrease of the ability to chemisorb hydrogen. The large Pb/Si surface atomic ratio in the MCM-41-supported palladium catalyst is explained, considering that lead is preferentially deposited outside the channels of this mesoporous solid.

The hydrogenation of alkynes was carried out at 298 K and 1 bar during 2 h. In none of the cases deactivation was observed. The hydrogenation products were the *cis*-isomers, the *trans*-isomers, and the saturated compounds. Figure 3 displays the evolution of the conversion level on time, in the 1-phenyl-1-pentyne hydrogenation for a representative catalyst. It can be seen that the conversion increases linearly with time, indicating a zero-order dependence on the concentration of the alkyne molecule. Even though the trends were similar for all the studied catalysts, significant differences in the catalytic activity was observed, with Pd/MCM-41 being the most active catalyst. A summary of the results, expressed as zero-order specific rate constant and turnover frequency (TOF), for the three studied reactions are given in table 3. It is remarkable that Pd/SiO_2 and Pd/MCM-41 catalysts exhibit much higher activity compared with the one supported on a silylated MCM-41 and with the Pb-poisoned, Pd-supported catalysts. With regard to Pd/MCM-41-Si, the observed behavior may be attributed to a limited access to the channels due to the presence of trimethylsilane groups incorporated in the silylation process, which are very voluminous and prevent the entrance of the reactants. On the other hand, the addition of lead produces a poisoning effect of the metallic phase, leading to a drastic decrease in the catalytic activity. In fact, the activity of the poisoned catalysts, expressed as zero-order constant rate, is approximately 30 times lower than that of the Pd-supported catalysts. This is attributed to a lower hydrogenation capacity of these solids, as it was inferred from the characterization results. The effect of palladium dispersion on the hydrogenation of 1-butyne has been widely studied, and it is known that changes in the metal dispersion, i.e., different particle sizes, and incorporation of lead also to changes in TOF and selectivity. However, this is not straightforward and results are often contradictory. Several authors [13–15] have reported a decrease in the specific activity as the particle size decreases, whereas others found the TOF to increase upon increasing metal dispersion [16]. Moreover, recent publications have disclosed a structure insensitivity reaction or only small changes in activity, but most of the studies agree with activity drop with an increase in dispersion. This apparent disagreement may be understood by considering that reactions have been carried out under different experimental conditions. As illustrated in table 3, the highest TOF is displayed by the catalyst that possesses the highest H/Pd ratio. No significant changes in particle size were exhibited by the catalysts supported on SiO_2 or MCM-41. However, the proportion of surface palladium atoms decreases upon lead incorporation, which destroy palladium ensembles and consequently decreases the hydrogenation ability. In fact, the Pb-Pd catalysts exhibit TOF values two or three times lower than the palladium counterpart. This change is not so large as the one that usually occurs in structure-sensitive reactions, in line with some of the previous work in alkyne hydrogenations [17–21]. In the Pd-silylated catalyst, that possesses a lower dispersion, activity is much lower compared with the other monometallic catalysts. The activity of Pb-Pd/MCM-41-Si is still

Table 3
Specific rate constant (*k*) and selectivity to the *cis*-isomer on Pd-supported catalysts

Catalysts	*k* (M min/g)			TOF (s^{-1})		
	Propyne	Butyne	Pentyne	Propyne	Butyne	Pentyne
Pd/SiO_2	0.058	0.086	0.122	73	109	154
Pd/MCM-41	0.098	0.178	0.229	82	150	193
Pd/MCM-41-Si	0.005	0.021	0.022	10	44	46
Pb-Pd/SiO_2	0.002	0.003	0.005	32	48	80
Pb-Pd/MCM-41	0.004	0.005	0.007	27	34	47
Pb-Pd/MCM-41-Si	0.001	0.002	0.003	18	35	53

Note: Conversion level, 10%.

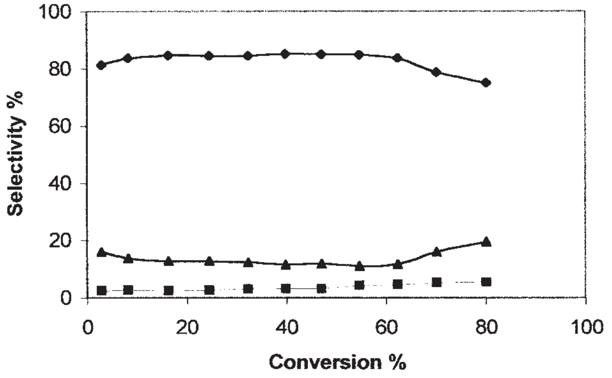

Figure 4. Selectivity to hydrogenated products in 1-phenyl-1-pentyne hydrogenation over Pd/MCM-41 catalyst. (◆), *cis*-1-phenyl-1-pentene; (■), *trans*-1-phenyl-1-pentene; (▲), 1-phenyl-1-pentane.

Table 4
Turnover frequency in hydrogenation of phenyl-alkynes on Pd-supported catalysts

Catalysts	Selectivity to *cis*-isomer[a] (%)		
	Propyne	Butyne	Pentyne
Pd/SiO_2	95	95	92
Pd/MCM-41	92	90	84
Pd/MCM-41-Si	90	69	55
$Pb\text{-}Pd/SiO_2$	98	52	46
Pb-Pd/MCM-41	92	71	65
Pb-Pd/MCM-41-Si	41	27	18

[a] At a conversion level of 10%.

lower because of the poisoning of the palladium surface atoms.

In the same table, a comparison of the activity data in the hydrogenation of different alkynes is reported. Although the changes in molecular size of the studied alkynes are small, a significant increase in both specific rate constant and TOF with increasing molecular size of the alkyne was observed. This may be attributed to the differences in the mobility of the molecules, being higher for smaller molecules. Therefore, the probability to react with hydrogen is higher for the larger molecules, as is the case for 1-phenyl-1-pentyne. Additionally, it is worth mentioning that this effect is still more important in the mesoporous solids. In fact, the reaction rate for the same probe molecule is much higher on this type of catalysts, and, therefore, the effect previously discussed is more important. These results are in agreement with previous results [22] in which the effect of the porosity of the solid has been discussed.

Figure 4 shows the evolution of selectivity during phenyl-alkyne hydrogenation for a representative Pd-supported catalyst. The main product is the *cis*-alkyne with a low proportion of *trans*-alkyne and alkane, respectively. The selectivity to the *cis*-isomer is rather constant up to approximately 60% of conversion and then it starts decreasing. Simultaneously, an increase in both the *trans*-isomers and the alkane derivative is observed. Similar behavior was exhibited by the other catalysts with some differences in the selectivity levels, especially in those samples with lower H/Pd ratio. In these later samples, under the same experimental conditions, the conversion was lower than 15% after 2–3 h of reaction. Table 4 summarizes the selectivity to the different hydrogenated products during the hydrogenation of the phenyl alkynes obtained at the same conversion level for the studied catalysts. The selectivity to the *cis*-isomers is in the range 86–95% for conversion levels 0–60% for Pd/SiO_2 and Pd/MCM-41 catalysts. The catalysts having lower catalytic activity displays also lower selectivity to this isomer. This may be explained considering that, being the highest, the activity is more likely to continue the hydrogenation reaction of alkyne to the overhydrogenated compound and partially to *trans*-isomer. 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 [23–24]. It is generally accepted that direct *trans*-isomers formation may occur via the addition of molecular hydrogenation to the adsorbed alkyne molecule [25]. The problem of stereoselectivity has been rarely addressed in recent years and only a few papers have disclosed results on the hydrogenations of internals alkynes [22,26,27].

4. Conclusions

The effect of the support and the incorporation of lead to palladium metal on the performance in the hydrogenation of acetylenics have been studied. It was found that a Pd/MCM-41 catalyst having a very narrow mesoporosity displays the best catalytic behavior compared with a silica support or a silylated MCM-41 sample. Confinement effects have been argued as a possible explanation. If this mesoporous solid is silylated, activity drops as a consequence of the limited access of the reactant molecule. Lead incorporation to the supported palladium catalyst produces a drastic decrease in the activity as a consequence of the poisoning of metallic palladium sites. The catalytic activity increases with the alkyne molecular size. The main hydrogenation product was the *cis*-alkene; only in the catalysts with lower activity, higher proportion of the overhydrogenated and *trans*-isomers appear.

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