A comparative study of Pd supported on MCM-41 and SiO$_2$ in the liquid phase hydrogenation of phenyl alkyl acetylenes mixtures

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Abstract

Competitive hydrogenation reactions between phenyl alkyl acetylenes over Pd/MCM-41 and Pd/SiO$_2$ catalysts have been studied. The catalysts were prepared by impregnation MCM-41 and SiO$_2$ with Pd(acac)$_2$ precursor, with metal content close to 1 wt.%. All the supports were characterised by nitrogen adsorption–desorption isotherms at 77 K, XRD, TGA measurements. The catalysts were characterized by H$_2$ and CO chemisorption, XPS and TEM measurements. Three competitive reaction systems 1-phenyl-1-pentyne/1-phenyl-1-propyne, 1-phenyl-1-pentyne/1-phenyl-1-butyne, 1-phenyl-1-butyne/1-phenyl-1-propyne have been examined. The results show that the competitive reaction results in an increase of the hydrogenation rate for phenyl alkyl acetylene with minor alkyl chain size in all studied systems. However, the 1-phenyl-1-pentyne/1-phenyl-1-propyne couple revealed a rate enhancement for 1-phenyl-1-propyne, but 1-pheny-l-pentyne single activity is higher than 1-phenyl-1-pentyne mixture, being the hydrogenation of 1-phenyl-1-propyne more favoured. Kinetic analysis of the reactions revealed that often the hydrogenation of the phenyl alkyl acetylenes is a zero order in a competitive environment. 1-Phenyl-1-propyne was very sensitive to the presence of the second phenyl alkyl acetylene. Competitive hydrogenation also increases the selectivity to the respective alkenes as can be expected from the competition for active sites.

1. Introduction

Different supports such as silica [1], alumina [2], mesostructured materials [3–10] and smectite clays [3–10] have been synthesized for use in fine chemistry. These supports are possible use in the stereospecific hydrogenation of phenyl alkyl acetylenes order to obtain higher activity and selectivity to the corresponding alkenes.

Although palladium catalysts are preferred for the selective partial hydrogenation of alkynes, they are usually used with a variety of modifiers to improve reaction selectivity. Metal salts, amines, amine oxides, sulfur compounds, hy-

droxides and carbon monoxide are among the others used modifiers [11]. For heterogeneous systems, the catalyst performance is strongly influence by: (i) the ability to get reactants to the active sites, (ii) to establish the optimum hydrogen to phenyl alkyl acetylene surface coverage, and (iii) the rapid removal of the hydrogenated products. These constitute the mass transfer limitations and can have an overriding impact on the ability to achieve selective hydrogenation.

On balance, palladium offers the best combination of activity and selectivity at reasonable cost, and for these reasons has become the basis of the most successful commercial alkynes superior hydrogenation catalysts. Because of their inherently high activity, these catalysts contain typically less than 0.5 wt.% of active metal to preserve selectivity even at higher alkyne conversion. Despite the

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prominence of these catalyst, other active metals are used in fine chemicals applications, e.g. reaction in 95% aqueous ethanol solution yields the P2-Ni(B) catalyst and selectivity in alkyne semihydrogenation has been demonstrated in the reaction of 3-hexyne to produce *cis*-3-hexene with 98% yield [12,13].

Although the hydrogenation selectivity is known to be sensitive to additives and catalyst preparation conditions, the origin of side reactions in hydrogenation reactions is still under discussion. In the semihydrogenation of phenyl acetylene, it was reported that treatment of the Lindlar catalyst with a variety of transition–metal compounds resulted in an improvement of the semihydrogenation selectivity [14]. Secondary modifiers are commonly used with Lindlar's catalyst. The usual secondary modifier is quinoline, which is reported to enhance the selectivity for the semihydrogenation of a variety of substituted acetylenes [11].

It has been tried to relate the activity of catalysts of Pd in the partial hydrogenation of phenyl alkyl acetylene, with the nature and porosity of the support. The most common support materials exploited commercially have been silica and, particularly, low surface area α-alumina, which combines high strength and low intrinsic chemical activity. As an example, the effect of surface area on the performance of an ethyne semihydrogenation catalyst, in this case high ethene selectivity is maintained up to a maximum support surface area of approximately 50 m^2/g catalyst [15]. There exists several reports in which the use of partial reducible supports may affects significantly the activity and the selectivity of different reactions, by the creation of interfacial sites [16,17]. The important effect of the support as molecular sieves has been pointed out in number of reactions in which the access of larger molecules inside the pore structure of the solids, mainly zeolites, plays an important role [18]. To overcome diffusion resistance, large pore supports are usually preferred and recent interest in heterogeneous catalysis has focused on the development of a new family of mesoporous MCM-41 materials discovered recently [19]. This type of supports has been reported to exhibits high activity, associated with high thioresistance for the hydrogenation of aromatics found in diesel fuels [20].

This work was undertaken with the aim to study the influence of the reactant molecular size, on the activity and selectivity in the stereoselective hydrogenation in liquid phase of phenyl alkyl acetylenes mixtures. Commercial silica and MCM-41 type (synthesised in the laboratory) have been used as supports of the Pd catalysts. Specific surface area was evaluated from the nitrogen adsorption isotherms, metal dispersion from H$_2$ and CO chemisorptions and TEM, XRD, TGA and XPS studies were as performed. The hydrogenations in liquid phase of the phenyl alkyl acetylenics (mixtures of 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. Chemicals

The cetyltrimethylammonium bromide (CTAB) (Aldrich Chemical Company), fumed silica (Sigma) and tetramethylammonium hydroxide (TMAOH) at 25% solution in water (Merck) were used for MCM-41 support synthesis. Substrates were of commercial origin (1-phenyl-1-propyne, 1-phenyl-1-butyne and 1-phenyl-1-pentyne (Aldrich 99% of purity) and used without further purification. The solvent tetrahydrofuran (THF) was dried and distilled under a nitrogen atmosphere. Hydrogen (99.995% purity, an AGA product) was used.

2.2. Supports and catalysts used

Two different supports were used: a commercial SiO$_2$ (BASF D11-11) and a mesoporous material type MCM-41. The synthesis of MCM-41 was performed using a standard procedure [19,21]. Basically, MCM-41 was prepared with the following gel of composition SiO$_2$:CTABr:TMAOH:H$_2$O = 1:0.15:0.26:24.3. The catalysts were prepared by the impregnation procedure using a slight excess of solution required to fill the pore volume of the supports with a solution of Pd(acac)$_2$ in toluene. The solids were dried at 373 K and calcined at 673 K under air flow for 4 h. The solids were labelled as 1% Pd/SiO$_2$, 1% Pd/MCM-41. Both catalysts were reduced in situ in hydrogen at 573 K for 1 h before their characterisation or catalytic evaluation.

2.3. Characterisation

X-ray diffraction (XRD) patterns were obtained on a Rigaku diffractometer using a Ni-filter and Cu Kα$_1$ radiation. Counts were accumulated every 0.02° (2θ) at a scan speed of 2θ 1° min^{-1}. Thermogravimetric analysis (TGA) of the supports were carried out in a Mettler Toledo TGA/SDTA851e apparatus in a temperature range from 273 to 873 K. 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 1–100 mmHg. The hydrogen uptake was evaluated from the irreversible amount of adsorbed H$_2$, as the difference between the first (total) and the second (reversible) isotherms in the pressure range 1–4 mmHg. TEM micrographs were obtained in a Jeol Model JEM-1200 EXII System.

Photoelectron spectra (XPS) were recorded using an Escalab 200R spectrometer provided with a hemispherical analyzer, operated in a constant pass energy mode and Mg Kα X-ray radiation (hν = 1253.6 eV) operated at 10 mA and 12 kV. The system was provided with a reaction cell, which

allows pre-treatment 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 ratio were estimated from the integrated intensities of Pd $3d_{5/2}$ and Si 2p lines after background subtraction and corrected by the atomic sensitivity factors. The line of Si 2p at 103.4 eV was used as an internal standard. Pd peaks were decomposed into several components assuming Gaussian–Lorentzian shapes.

2.4. Catalytic experiments

The competitive semihydrogenation in liquid-phase of the phenyl alkyl acetylene mixtures (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. For each measurement, 25 mg of the powdered catalyst was placed in the reaction reactor. Hydrogenation was conducted under efficient stirring (1400 rpm) to eliminate diffusional control. The total volume used was 15 ml. A phenyl–acetylene mixture molar ratio was 1:1 in all experiments. A substrate-mixture:Pd molar ratio of 5000 was 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 solvent (dried THF) was injected and the phenyl alkyl acetylenes mixtures were fed under constant stirring. Samples were taken periodically and analysed by a Star VARIAN 3400-CX gas chromatograph provided with a capillary column DB-Wax (0.53 mm; 30 m) and flame ionisation detector (FID). The reactions products were identified with a Shimadzu QP5050A GC-MS apparatus.

3. Results and discussion

3.1. Catalyst characterization

Powder XRD and N_2 sorption studies are regularly used to assess the quality and structural ordering of MCM-41 materials. It is essential that both techniques be used to obtain the fullest information regarding mesopores ordering in these materials. Nitrogen adsorption on the MCM-41 sample shows typical type IV isotherms [22]. The sharp inflection at relative pressures >0.3 is characteristic of capillary condensation within uniform mesopores. The sharpness of the step reflects the uniformity of the pores [23–25]. The second step in the isotherm at relative pressures >0.9, which is observed for MCM-41 sample, is attributed to the condensation of nitrogen in the depressions of rough surfaces or between small MCM-41 particles. The structural properties of supports were reported in our previous work [21] and reproduced here in Table 1. The BET surface areas of the Pd exchanged catalysts show that only slight changes occur in the textural characteristic of the supports. This change in the surface areas of the catalysts it indicates that the in-

troduction of Pd does not affects significantly the original structure.

The XRD patterns of the calcined and non calcined MCM-41 supports (Fig. 1) showed four characteristic peaks that can be indexed on a hexagonal lattice of a typical mesoporous MCM-41 material as (1 0 0), (1 1 0), (2 0 0) and (2 1 0) planes. The diffraction peak related to the (1 0 0) plane possesses higher intensity for synthesised samples, which can be taken as an indication of higher ordering of the mesoporous channels [19]. XRD data of Pd/MCM-41 show no structural changes during the preparation of the catalyst in agreement with physisorption results. TG analysis of MCM-41 support exhibited a higher weight loss at temperatures up to ca. 373 K, which can be attributed to the evolution of physically adsorbed water [26,27] and therefore indicates a relatively hydrophilic character of its surface. At higher temperatures, the TG analysis curve was very flat, especially up to ca. 813 K, showing that there is no appreciable condensation of silanol group on the surface of the material [26,27]. The TG analysis confirms that at 813 K the template molecules inside of the channels of the MCM-41 support are completely removed.

Fig. 2a shows a representative TEM micrograph of the calcined MCM-41 materials. Typical shapes of these solids with a regular hexagonal array of mesoporous channels can be observed. Fig. 2b shows a representative electron diffraction pattern for MCM-41 support; this micrograph confirms the hexagonal packing and the regularity of the pore system characteristics of this material [28].

Table 1
Characteristic of the catalysts used

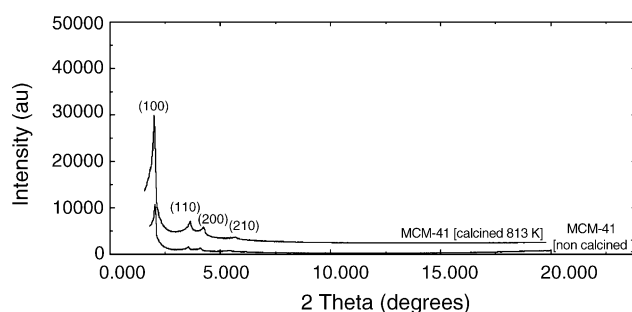| Catalysts	S_{BET} (m²/g)	r_p (Å)	V_p (cm³/g)	a_0 (Å)
1% Pd/MCM-41	984	22	0.89	46
1% Pd/SiO₂	85	80	0.16	–

Fig. 1. X-ray diffraction patterns of the synthesised MCM-41 samples.

Table 2
H/Pd and CO/Pd ratios obtained from chemisorption data and metal particle size of Pd-supported catalysts

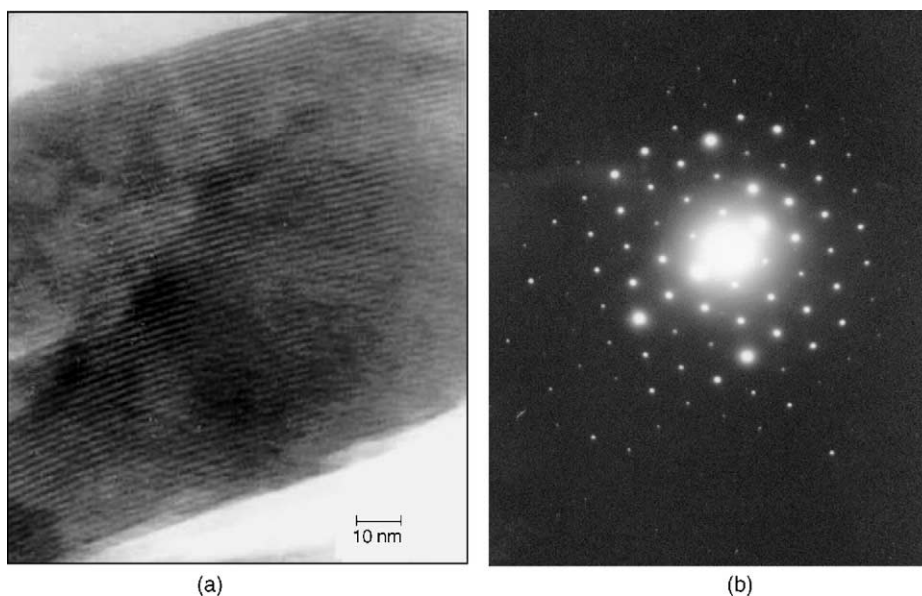| Catalysts	H/Pd	CO/Pd	d_{H_2} (nm)	d_{CO} (nm)	d_{TEM} (nm)
1% Pd/SiO₂	0.14	0.14	6.7	6.7	4.0
1% Pd/MCM-41	0.21	0.13	4.5	7.2	3.2

Fig. 2. (a) Transmission electron micrograph of MCM-41; (b) electron diffraction of MCM-41.

Table 2 summarizes H_2 and CO adsorption data for the catalysts used in the semihydrogenation of phenyl alkyl acetylenes mixtures. The H/Pd ratio of 1% Pd/SiO_2 catalyst is lower than that of 1% Pd/MCM-41 catalyst. This behaviour may be explained assuming that during the reduction of the precursor, the confinement inside the channel provide to the Pd particles more resistance to sinterisation during temperature reduction under H_2 flow. The H/Pd ratios reasonably agree with the CO/Pd ratios and the observed differences may be explained taking into account the difficulty to determine a precise stoichiometry for the adsorption of CO on Pd particles. Some authors have studied the different forms of adsorption from the CO over 1% Pd/SiO_2 to different reduction temperatures by IR-FT. They observed four adsorption modes of CO, linear, compressed bridged, isolated bridged and tricoordinated bonds [29,30]. The bands for the multiple bound CO, including the bridged and tricoordinated types, are usually overlapped and characterized by peaks located below 2000 cm^{-1}.

To compare more directly the Pd dispersion of catalysts, we have obtained TEM micrograph of the catalysts, either supported on SiO_2 and MCM-41 supports. A very narrow palladium particle size distribution was observed on both supports. The values of the average metal particle size obtained by TEM showed a higher value for 1% Pd/SiO_2 catalyst, indicating lower Pd dispersion in agreement with chemisorption values (see Table 2).

Fig. 3 shows the Pd 3d core level spectra of the studied catalysts. Both samples display similar feature having signals of Pd $3d_{5/2}$ of 335.0 and 334.8 eV for 1% Pd/SiO_2 and a 1% Pd/MCM-41, respectively (Table 3). These values are close to that expected for Pd^0 (eV). The slight shift observed in the catalysts respect to metallic palladium may be explained considering that the binding energy is affected not only by
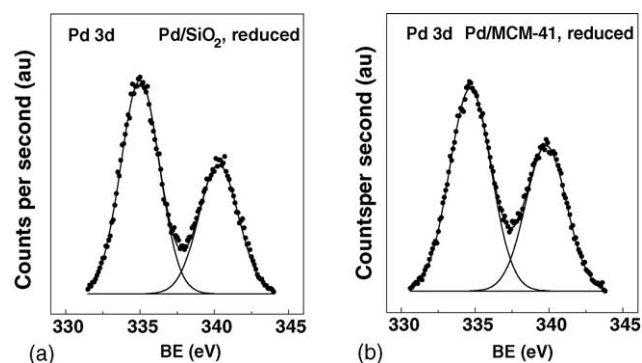

Fig. 3. XP spectra of: (a) Pd $3d_{5/2}$ of Pd/SiO_2; (b) Pd $3d_{5/2}$ of 1% Pd/MCM-41 core-levels of the reduced catalysts.

the electronic interaction of the metal with other components but also by the particle size of the metal crystallites. Thus, Takasu et al. [31] have reported a decreased in 1.6 eV in the BE of Pd $3d_{5/2}$ in 1% Pd/SiO_2 catalyst when the particle size increased within a range smaller than 5 nm. Similar trends have been reported for Pd and Pd–Ti particles supported in SiO_2 [27]. Taking into account the H/Pd ratios and the metal particle sizes obtained by TEM given in Table 2, only few changes in BE should be expected. Additionally, the Pd/Si atomic surface ratios obtained by XPS slowed comparable values for both samples, in agreement with the chemisorption and TEM results.

Table 3
Binding energies (eV) of core-levels and surface atomic ratios of reduced Pd-supported catalysts

Catalyst	BE Pd $3d_{5/2}$	Pd/Si atom
1% Pd/SiO_2	335.0	0.014
1% Pd/MCM-41	334.8	0.013

3.2. Competitive hydrogenations

Three competitive reaction systems were studied, 1-phenyl-1-pentyne/1-phenyl-1-propyne, 1-phenyl-1-pentyne/1-phenyl-1-butyne, 1-phenyl-1-butyne/1-phenyl-1-propyne. The hydrogenation of phenyl alkyl acetylenes mixture was carried out at 298 K and 1 bar of H_2 during 2 h. No deactivation was observed during the reaction. The single systems were also examined as references [21]. In all cases, the main product was the *cis*-alkene with a low proportion of *trans*-alkene and the saturated compound, respectively. Phenyl alkyl acetylenes can be classified as an internal alkyne and hence the competitive hydrogenation of phenyl alkyl acetylenes can be treated similarly as the hydrogenation of other internal alkynes. The internal alkynes upon hydrogenation may yield to the corresponding *cis*-alkenes with high selectivity [32]. The problem of stereoselectivity has been rarely addressed, only few papers have disclosed results on the hydrogenation of internal alkynes [33,34]. The best performance has been observed with Pd–B/SiO$_2$ catalyst showing high selectivity which is maintained after the disappearance of the starting alkyne.

To minimize mass transfer limitation the catalysts were used as powdered samples with small catalyst grain ($<200\,\mu$m) and the stirring was 1400 rpm. In previous work, we have demonstrated that under these conditions, the reaction takes place under kinetic control. The initial reaction rates values were evaluated from the dependence $[A] = kt$, where $[A]$ = phenyl alkyl acetylene concentration, k = rate constant and t = time and afterwards used for the calculation of the relative adsorption coefficients. The reactions were almost of zero order dependence on the substrates concentrations in the phenyl alkyl acetylenes mixtures systems in agreement with recent studies over mesoporous materials [24], this behaviour was observed even at high conversion levels (see Fig. 4).
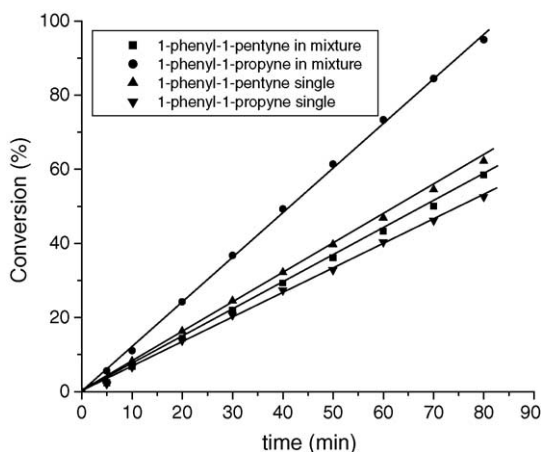

Fig. 4. Evolution of conversion level on time for 1-phenyl-1-pentyne/1-phenyl-1-propyne system over 1% Pd/MCM-41 catalyst, $T = 298$ K, $P_{H_2} = 1$ bar, phenyl alkyl acetylene molar ratio 1:1.

Fig. 4 displays the evolution of the conversion level with time on stream for the hydrogenation of the pure 1-phenyl-1-pentyne, 1-phenyl-1-propyne, and the hydrogenation of each substrate in the mixture of the 1-phenyl-1-pentyne/1-phenyl-1-propyne system on 1% Pd/MCM-41 catalyst. It can be seen that the conversion increases linearly with time for all systems, indicating a zero order dependence on the concentration of the phenyl alkyl acetylene molecule in the single or mixture system. Eventhough the trends were similar for all the studied catalysts, it can be seen from Fig. 4 that the rate of hydrogenation of 1-phenyl-1-propyne was increased by a factor of two approximately, but the rate of 1-phenyl-1-pentyne hydrogenation did not have greater changes compared with 1-phenyl-1-pentyne single activity than in 1-phenyl-1-pentyne mixture hydrogenation. The overall increase in the reaction rate for 1-phenyl-1-propyne may be due to an increase in the effective hydrogen concentration at the surface and the strong adsorption of the alkyne on the metallic particle. The trends were similar for all phenyl alkyl acetylene with minor alkyl chain size in all studied systems. The zero order kinetics observed for both 1-phenyl-1-pentyne and 1-phenyl-1-propyne during the competitive reaction indicates that the phenyl alkyl acetylenes are strongly adsorbed having a high surface coverage in agreement with other results observed in competitive reactions during alkyne hydrogenations [35]. The authors have attributed this behaviour only holds if the adsorption of the alkynes does not subscribe to a random two-site adsorption, it is necessary that some sites only adsorb some of two alkynes in the mixture, so that the co-adsorption removes more potential hydrogen adsorption sites. However, they concluded that it is unlikely that the mode of adsorption is the sole defining factor in the alkyne reactivity. Similar explanations have been given by Jackson and Kelly [36] for the hydrogenation of pentynes on Pd/C catalyst. They found, that, in contrast to the classical expectation, the internal alkyne is hydrogenated faster than the terminal alkyne. To explain their unusual observation, they considered the possible adsorption modes for the alkynes: both parallel and perpendicular for the terminal alkyne, whereas only the parallel mode is involved in the internal alkyne.

In present study, we considered the adsorption strength of internal alkynes. It is well known that the internal alkynes have strong complexing abilities and this is one of the reasons for the high semihydrogenation selectivity over Pd. The strong adsorption of the alkyne prevents the readsorption of the alkene and hence the consecutive hydrogen addition cannot take place [37,38].

A dramatically different behaviour occurs when the alkyl chain is diminished: the conversion of 1-phenyl-1-propyne hydrogenation is significantly enhanced compared than that observed when 1-phenyl-1-propyne is hydrogenated in the absence of 1-phenyl-1-pentyne [21], while the conversion of 1-phenyl-1-propyne hydrogenation is increased approximately 50%. A similar behaviour has been observed in a competitive reaction with internal and terminal alkynes [35,36]. These authors explain this enhancement in the hydrogenation

rate of alkyne by an increase in the surface hydrogen concentration. This type of enhancement may be similar to that observed in the chiral hydrogenation catalysis where it has been proposed that increasing the hydrogen transfer through the addition of a modifier can result in a significant increase in the rate of reaction [39]. For all the systems, it has been clearly demonstrated that the values of conversion of competitive hydrogenations were always significantly shifted in favour of the 1-phenyl-1-propyne molecules on both tested catalysts. In contrast, the 1-phenyl-1-propyne is preferentially hydrogenated in the presence of other phenyl alkyl acetylenes over both catalysts as the rates of the individual hydrogenations indicate.

The result of the kinetic studies in the competitive mechanism comes from the relative adsorption coefficients of the individual alkynes, as it has been obtained by the use of the Rader–Smith equation [40]:

$$\frac{\log(c_1/c_1^0)}{\log(c_2/c_2^0)} = \frac{k_1 K_1}{k_2 K_2} = S_{1,2}$$

being ($S_{1,2}$) the competitive hydrogenations, (k_1/k_2) the rate constant ratio, c the instantaneous concentration, c^0 the initial concentration, (K_1/K_2) the adsorption coefficient and 1 and 2 subscript the compounds. The values obtained from the catalytic experiments of competitive hydrogenations in double systems constitute a basis for the discussion of the molecule effect on the activity and adsorptivity of phenyl alkyl acetylenes mixtures. The plot $\log(c_1/c_1^0)$ versus $\log(c_2/c_2^0)$ are linear for all systems indicating competitive adsorption. This behaviour is in agreement with other studies of alkynes mixtures [35,38,41,42]. Fig. 5 shows the $\log(c_1/c_1^0)$ versus $\log(c_2/c_2^0)$ plot according Rader–Smith procedure, from the slop, the $S_{1,2}$ values for the different systems may be obtained (see Table 4). Using the initial reaction rate k_1 and k_2 and the selectivity values $S_{1,2}$, the relative adsorption coefficients K_1/K_2 were calculated. For the 1-phenyl-1-pentyne/1-phenyl-1-propyne mixture a ratio K_1/K_2 of 0.56 on 1% Pd/MCM-41 catalyst was obtained, confirming the stronger adsorption of the 1-phenyl-1-propyne. Similar behaviour was observed for 1% Pd/SiO$_2$ catalyst. In the other mixtures, the effect is not so dramatic; indeed the K_1/K_2 ratios was close to 1 (see Table 4). Table 4 clearly demonstrates that the values of selectivities ($S_{1,2}$) of competitive hydrogenations in the mixture systems is favoured
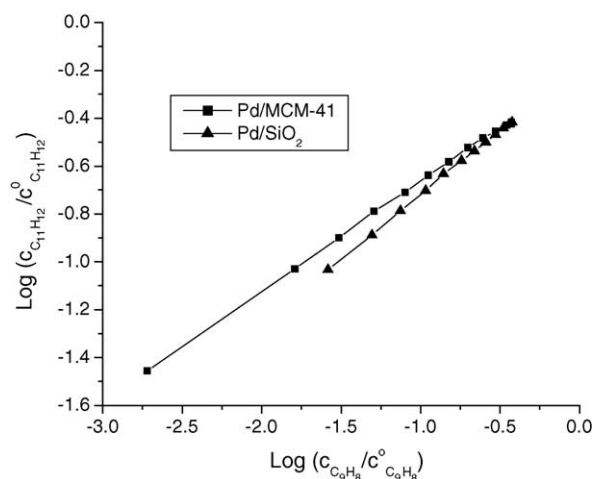

Fig. 5. Dependence of the concentrations of 1-phenyl-1-pentyne and 1-phenyl-1-propyne during competitive hydrogenations over 1% Pd/MCM-41 catalyst, $T = 298$ K, $P_{H_2} = 1$ bar.

for the phenyl alkyl acetylenes molecule with shorter length chain alkyl on both catalysts. The significant differences in the selectivity with respect to the other systems were observed for 1-phenyl-1-pentyne/1-phenyl-1-propyne system on both tested catalysts. The small differences in the values of selectivities and adsorption coefficients becomes from the effect of the chain alkyl size.

The parameter of selectivity ($S_{1,2}$), adsorptivity (K_1/K_2) in both 1% Pd/MCM-41 and 1% Pd/SiO$_2$ catalysts were similar for all studied cases. This behaviour was not be expected for Pd catalyst support in MCM-41 with respect to SiO$_2$ due to broader porosity, ordered mesostructured and better dispersion of Pd in MCM-41 like obtained in previous works [21]. For singles hydrogenations MCM-41 supports shows superior activity over SiO$_2$ supports [21] in the hydrogenation of phenyl alkyl acetylenes under identical experimental conditions, but the effect of ordered mesoporous channels in the competitive hydrogenation of phenyl alkyl acetylenes is reflected in the increases of the activity of phenyl alkyl acetylenes with minor alkyl chain size as the case of 1-phenyl-1-propyne. In resume, mesostructured supports such as MCM-41 give satisfactory results for competitive hydrogenation of phenyl alkyl acetylenes.

On Pd catalysts, the competitive semihydrogenation of phenyl alkyl acetylenes basically results in the predominant

Table 4
Selectivities of competitive hydrogenations and adsorption coefficients for all systems studied

Substrate		K_1/K_2[a]		k_1/k_2[b]		$S_{1,2}$[c]	
1	2	Pd/MCM-41	Pd/SiO$_2$	Pd/MCM-41	Pd/SiO$_2$	Pd/MCM-41	Pd/SiO$_2$
C$_{11}$H$_{12}$	C$_9$H$_8$	0.56	0.58	0.80	0.90	0.45	0.53
C$_{10}$H$_{10}$	C$_9$H$_8$	1.00	0.91	0.75	0.92	0.75	0.84
C$_{11}$H$_{12}$	C$_{10}$H$_{10}$	0.94	0.88	0.76	0.85	0.72	0.75

[a] Adsorption coefficients ratio.

[b] Rate constant ratio.

[c] Selectivity of competitive reactions: C$_9$H$_8$: 1-phenyl-1-propyne; C$_{10}$H$_{10}$: 1-phenyl-1-butyne; C$_{11}$H$_{12}$: 1-phenyl-1-pentyne.

Table 5
Selectivity to *cis*-isomer for competitive hydrogenation of phenyl alkyl acetylenes mixtures over Pd/MCM-41 catalyst

Catalysts	Selectivity to *cis*-isomer (%)[a] systems					
	$C_{11}H_{12}/C_9H_8$		$C_{10}H_{10}/C_9H_8$		$C_{11}H_{12}/C_{10}H_{10}$	
	cis-$C_{11}H_{14}$	*cis*-C_9H_{10}	*cis*-$C_{10}H_{12}$	*cis*-C_9H_{10}	*cis*-$C_{11}H_{14}$	*cis*-$C_{10}H_{12}$
1% Pd/MCM-41	90	88	91	93	90	91
1% Pd/SiO$_2$	93	90	94	96	94	95

[a] Conversion level 20%; C_9H_8: 1-phenyl-1-propyne, $C_{10}H_{10}$: 1-phenyl-1-butyne, $C_{11}H_{12}$: 1-phenyl-1-pentyne; *cis*-$C_{11}H_{14}$: *cis*-1-phenyl-pentene, *cis*-C_9H_{10}: *cis*-1-phenyl-1-propene, *cis*-$C_{10}H_{12}$: *cis*-1-phenyl-1-butene.

formation of the *cis*-alkene stereoisomer (see Table 5) for all systems, which is attributed to the associative adsorption of the reactant and the consecutive addition of two adsorbed hydrogen from below the axis of the triple bond [43]. On the other hand, *trans*-alkene formation is generally related to the addition of molecular hydrogen from above the axis of the unsaturation. For the transformations of internal alkynes, *trans*-alkenes are always formed, either as initial products or via *cis*–*trans* isomerization [44], this being accompanied by alkane production through overhydrogenation [44]. The finding that the stereoselectivity for the formation of the main reaction product *cis*-alkene was high ($\approx$88–96%) for all the studied Pd-supported catalysts. The low extent of overhydrogenation is also indicative that the re-adsorption of the *cis*-alkene on the Pd surface was rather insignificant [43].

4. Conclusions

The obtained results show that, in general, the competitive reaction lead to in an increase of the hydrogenation rate for phenyl alkyl acetylene with shorter alkyl chain size. This can be explained by an increase in the strongly adsorbed alkyne molecule in the competitive hydrogenation reaction. For the 1-phenyl-1-pentyne/1-phenyl-1-propyne system revealed than that the hydrogenation of 1-phenyl-1-propyne more favoured. This is proposed to be a consequence of hydrogen transfer to the surface with each adsorbed phenyl alkyl acetylene acting as an enhancement of the hydrogen transfer agent to the other. Kinetic analysis of the reactions revealed that often the hydrogenation of the phenyl alkyl acetylenes is a zero order with respect to the alkyne in a competitive environment. The 1-phenyl-1-propyne was very sensitive to the presence of the second phenyl alkyl acetylene. Competitive hydrogenation increases selectivity to the respective alkenes as can be expected from the competition for sites.

Acknowledgements

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