

Mesostructured silicas as supports for palladium-catalyzed hydrogenation of phenyl acetylene and 1-phenyl-1-hexyne to alkenes

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Abstract

The stereoselective hydrogenation of phenyl acetylene and 1-phenyl-1-hexyne at 298 K and atmospheric pressure of H₂ over Pd catalysts supported on mesostructured silica was studied. The catalysts were prepared by the impregnation of HMS and MSU-X silicas with 3-D wormhole framework structures and MCM-41 silica with a 1-D hexagonal framework using a toluene solution of Pd(acac)₂ to obtain a metal content close to 1 wt.%. All the supports were characterised by nitrogen adsorption–desorption isotherms at 77 K and XRD. The catalysts were characterized by H₂ chemisorption and TEM measurements. The reactions were found to be zero order with respect to the phenyl acetylene and 1-phenyl-1-hexyne concentration. Each catalyst presented a different catalytic performance. The 1%Pd/HMS catalyst was the most active in comparison with the 1%Pd/MSU-X and 1%Pd/MCM-41 catalysts. This superior performance in the case of the HMS support was attributed to the presence of interconnected framework channels and textural mesoporosity that can increase the accessibility of the Pd centers to a greater extent than the more monolithic MSU-X and MCM-41 supports. All catalysts displayed high selectivity to styrene and *cis*-1-phenyl-1-hexene compounds.
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1. Introduction

Semi-hydrogenation of alkynes is a versatile reaction widely used in organic synthesis [1] and often performed by noble metal supported catalysts [2]. In order to obtain higher selectivity and activity different supports matrices such as silica [3,4], carbon [5,6], and mesostructured MCM-41 silica [7,8] have been used. Although zeolites and pillared clays have been successfully used as supports of palladium catalysts for the production of fine organic chemicals [9–13], they have limited utility for the transformations of large molecules in the liquid state due to diffusion limitations caused by the restricted pore sizes.

Mesostructured silica with pores in the 2–5 nm range have been recognised as potentially superior supports over zeolites

and pillared clays for stereo-specific hydrogenation reactions partly due to their large pore size, which offers the possibility of minimizing diffusion limitations. Indeed, 1%Pd/MCM-41 has been shown to be an effective catalyst for the reduction of phenyl alkyl acetylene to *cis*-alkene [8]. 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 HMS and MSU-X silicas with wormhole framework structures [14–18]. HMS silica has been reported to exhibit a higher olefin adsorption capacity than exhibited by the corresponding alkanes. The higher affinity of the HMS framework for propylene over propane was verified by heats of adsorption for propylene that are significantly higher than for propane [19].

It was of interest in the present work to verify the catalytic properties of these mesostructured silica supports for the selective hydrogenation of alkynes, a reaction, which also is of industrial interest in fine chemical synthesis. Indeed, the complete elimination of alkynes from alkene feed stocks via selective

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hydrogenation is an important process in the polymer industry [20]. Pd catalysts supported on low surface area alumina are usually employed in the industrial process, but there has been renewed interest in supported palladium catalysts [21,22] in an effort to find more selective processes [23,24]. Several workers have studied the selective hydrogenation of alkynes to alkenes not only from the theoretical point of view, but also for industrial utilization, particularly in the selective elimination of low amounts of alkynes from alkenic fractions. Phenyl acetylene is the commonly studied substrate for hydrogenation in the liquid phase, and is often used as a probe molecule to compare catalytic activity.

The catalytic hydrogenation of alkynes is the easiest of all hydrogenation reactions, generally taking place in the presence of all other functional groups including conjugated dienes and aromatic nitro groups. Alkyne hydrogenation is enhanced if the triple bond is terminal. The complete hydrogenation of alkynes to saturated compounds occurs on all common hydrogenation catalysts at room temperature and atmospheric pressure. This reaction, and the related semi-hydrogenation to produce alkenes, is important in synthetic procedures because the acetylenic group can participate in a wide variety of substitution reactions, and thus can join two segments of a carbon chain to produce a variety of aliphatic species. The selective modification of the triple bond to form either a double or single bond further enhances the synthetic utility of acetylenic materials. The selective hydrogenation of a triple bond to give an alkene without concomitant positional or geometric isomerisation is particularly important in synthetic procedures and many industrial processes. In the absence of any isomerisation, selective partial hydrogenation of a di-substituted alkyne produces the *cis*-alkene. Small amounts of the *trans*-alkene are sometimes formed in these reactions, but catalytic processes do not lead to the production of the *trans*-olefin as the primary product.

The present work was undertaken with the aim to study the influence of mesostructured silicas supports on the activity

and the selectivity of Pd-catalysts for the liquid phase stereoselective hydrogenation of phenyl acetylene and 1-phenyl-1-hexyne (Fig. 1). In addition to hexagonal MCM-41 with one-dimensional framework pores, we have included in the study HMS and MSU-X mesostructures, which have wormhole and hexagonal framework structures, respectively. Specific surface areas were determined from the nitrogen adsorption isotherms, and metal dispersion from H₂ chemisorption. TEM and XRD studies were also performed. The liquid phase hydrogenation phase of phenyl acetylene and 1-phenyl-1-hexyne was performed at 298 K, 1 bar using tetrahydrofuran (THF) as solvent.

2. Experimental

2.1. Materials

Phenyl acetylene and 1-phenyl-1-hexyne were obtained from Aldrich and used without further purification. The solvent tetrahydrofuran (THF) was obtained from Aldrich. THF was dried with sodium wires and distilled under a nitrogen atmosphere before use. Fumed silica (Sigma), cetyltrimethylammonium bromide (CTAB) (Aldrich), tetramethylammonium hydroxide (TMAOH) at 25% solution in water (MERCK), tetraethylorthosilicate (TEOS) (Aldrich), dodecylamine (DDA) (Aldrich), and decaoxyethylene cetyl ether (Brij 56) (Aldrich) were used for support synthesis, and hydrogen (99.995% purity, an AGA product) was used.

2.2. MCM-41 silica

The synthesis of hexagonal MCM-41 was performed using a standard procedure [25]. Basically, MCM-41 was prepared with gel of the composition SiO₂:CTAB:TMAOH:H₂O = 1:0.15:0.26:24.3. A mixture of fumed silica, cetyltrimethylammonium bromide, trimethylammonium hydroxide, and water was stirred at room temperature for 1 h. The synthesis gel was

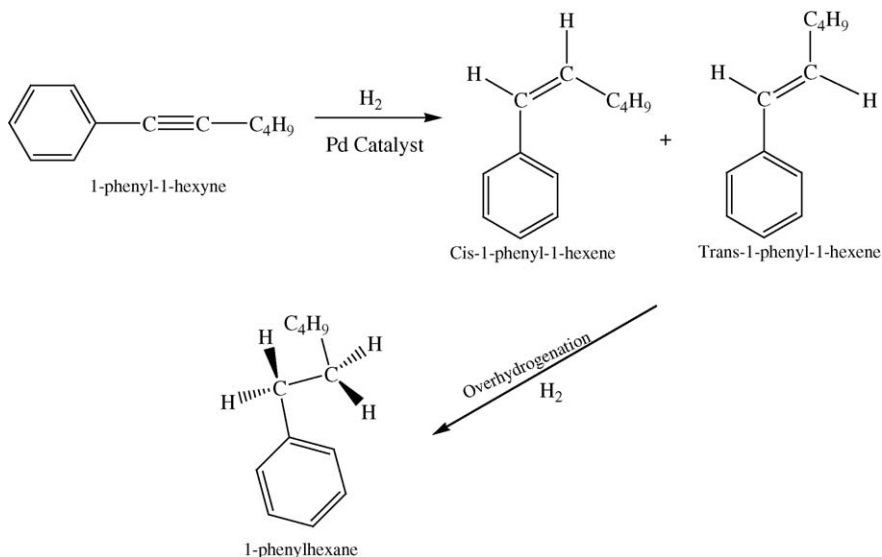


Fig. 1. Reaction diagram for the stereoselective hydrogenation of 1-phenyl-1-hexyne.

heated at 100 °C for 24 h in an autoclave to obtain hexagonal MCM-41 silica. The final product was filtered, washed, dried at room temperature, and calcined in nitrogen and air at 540 °C for 6 h to remove the surfactant.

2.3. MSU-X silica

This mesostructured silica with a wormhole framework structure was prepared as follows. A 10 wt.% of a micellar solution was prepared by dissolving decaoxyethylene cetyl ether (Brij 56) in distilled water. Sulphuric acid was then added to adjust the pH to a value of 2. After homogenization at 70 °C, TEOS was added drop-by-drop, and stirred further for 1 h. Hydrothermal treatment was performed at 40 °C for 3 days. The surfactant/silica molar ratio was 0.50. The recovered gel was then extracted with ethanol using a Soxhlet apparatus to eliminate the remaining surfactant molecules in the porous structure, and then dried under air at room temperature [26,27].

2.4. HMS silica

A second silica mesostructure with a wormhole framework structure, denoted HMS, was prepared according to previously reported methods [18]. Dodecylamine (DDA, 4.9 mmol) was dissolved in 5 ml of ethanol, and 45 ml of H₂O was then added to obtain a 90:10 (v/v) H₂O/EtOH solution of the surfactant. The surfactant solution was heated to the desired reaction temperature, and tetraethyl orthosilicate (TEOS, 19.6 mmol) was added to give a reaction mixture with an I°/S° ratio of 4. The reaction flask was sealed and shaken at 220 rpm in a heated water bath at the desired synthesis temperature, 60 °C for 20 h. The resulting white precipitates were filtered out, washed with copious amounts of H₂O, and allowed to air dry at room temperature for 24 h. The surfactant was removed by calcination in air at 600 °C for 4 h.

2.5. Catalysts

Calcined forms of mesostructured HMS, MSU-X and MCM-41 silicas were impregnated 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 amount required to obtain 1 wt.% of Pd. The catalysts were dried at 373 K and calcined at 673 K under air flow for 4 h. The catalysts were labelled as 1%Pd/HMS, 1%Pd/MSU-X and 1%Pd/MCM-41. The catalysts were reduced in situ in hydrogen at 573 K for 1 h prior to their characterisation or catalytic evaluation.

2.6. Characterisation

Specific area and porosity were obtained from nitrogen adsorption–desorption isotherms at 77 K performed in an automatic Micromeritics apparatus Model ASAP 2010 in the 0.05–0.995 relative pressure range. BET surface areas were calculated from a linear part of the BET plot according to IUPAC recommendations. Pore-size distributions were calculated from the N₂ adsorption branch using the Horvath–Kawazoe model.

Powder X-ray diffraction patterns were measured using Cu-K α radiation ($\lambda = 1.542 \text{ \AA}$) and a Rigaku diffractometer equipped with a rotating anode operated at 45 kV and 100 mA. Counts were accumulated every 0.02° (2θ) at a scan speed of 1° $2\theta \text{ min}^{-1}$.

Metal dispersion was determined by H₂ chemisorption in an automatic Micromeritics apparatus Model ASAP 2010. Hydrogen chemisorption was carried out at 343 K in the pressure range 1–100 mmHg. The hydrogen uptake was evaluated from the irreversible amount of adsorbed H₂ as determined by the difference between the first (total) and the second (reversible) isotherms. TEM micrographs were obtained in a Jeol Model JEM-1200 EXII System. The specimen was loaded onto a holey carbon film that was supported on a copper grid by dipping the grid into a sample suspension in ethanol. The catalysts samples were prepared by the extractive replica procedure.

2.7. Catalytic experiments

Semi-hydrogenation in liquid-phase of phenyl acetylene and 1-phenyl-1-hexyne was performed in a batch reactor at 298 K and 1 bar of H₂ pressure. In each measurement, 10 mg of the powdered 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. A molar ratio substrate: Pd of 2500 was used. Prior to the reaction, the sample was reduced at 573 K during 1 h in H₂ flow and cooled to the reaction temperature. Then, the solvent (dried THF) was injected and the substrates were fed under constant stirring. Samples were taken periodically and analysed by a Star VARIAN 3400-CX gas chromatograph with a capillary column DB-Wax (0.53 mm, 30 m) and flame ionisation detector (FID). The reaction products were identified with a Shimadzu QP5050A GC-MS apparatus.

3. Results and discussion

3.1. Structural and textural properties of the supports

The XRD patterns for HMS, MSU-X and MCM-41 silica mesostructures are presented in Fig. 2. The MCM-41 mesophase exhibits four hkl diffraction lines consistent with the expected hexagonal framework structure. The diffraction peak related to the (1 0 0) plane exhibits the highest intensity among all of the synthesised samples, which can be taken as an indication of the higher long range ordering of the mesoporous channels [25]. The wormhole framework of HMS exhibits a single diffraction line. For the MSU-X sample, the picture is different. In addition to the main reflection peak at low angle 2θ , the secondary reflections cannot be well distinguished, reflecting less ordering and homogeneity in the sample (Fig. 2) in comparison to MCM-41 and tending to a wormhole structure. TEM images (Fig. 3) verify the disordered channel arrangement and wormhole structure assignments for the MSU-X and HMS mesophases, as well as the hexagonal framework structure for MCM-41 material. The XRD patterns of the Pd catalysts indicated the retention of the framework structure after Pd incorporation.

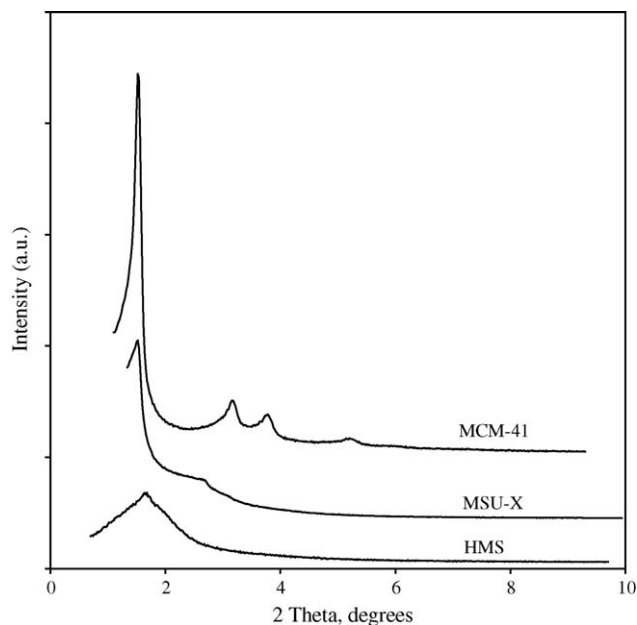


Fig. 2. XRD patterns of the silicate mesophases.

Table 1
Textural properties of the silicate mesophases

Sample	d_{100} (nm)	BET (m^2/g)	Pore diameter HK (nm)	Wall thickness ^a (nm)	V_T^b (cc/g)
HMS	4.5	910	3.2	1.3	0.9
MSU-X	5.8	1086	5.1	0.7	1.4
MCM-41	4.1	1469	3.3	0.8	2.4

^a Wall thickness calculated by subtracting the HK pore diameter from the correlation distance as determined by X-ray diffraction.

^b V_T , total volume obtained from the volume of N_2 adsorbed at $0.99 P/P_0$.

The textural properties of the silicate mesophases are provided in Table 1. All the isotherms are type IV, characteristic of mesoporous compounds, with a type H1 hysteresis loop [28]. The capillary condensation occurs at different P/P_0 values for the MSU-X sample, indicative of variable pore size. The surface areas, as determined by fitting the BET equation to nitrogen adsorption isotherms in the partial pressure region below 0.30, decreased in the order MCM-41 > HMS > MSU-X. The BET surface areas of the Pd catalysts show that only small changes occur in the textural characteristics. It can be concluded that Pd

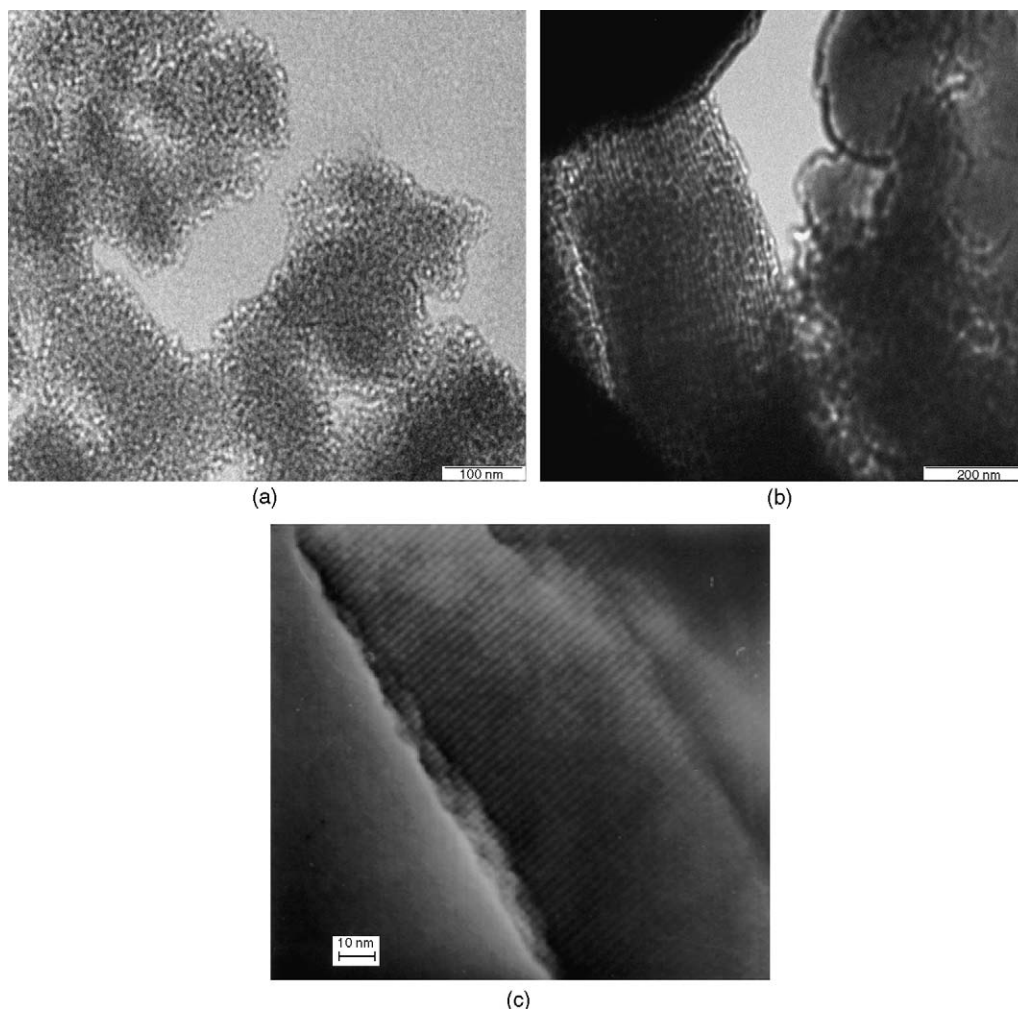


Fig. 3. Transmission electron micrograph of mesostructured supports (a) HMS, (b) MSU-X and (c) MCM-41.

Table 2

H/Pd ratio obtained from chemisorption data and metal particle size of Pd-supported catalysts

Catalysts	H/Pd	d_{H_2} (nm)	d_{TEM} (nm)
1%Pd/HMS	0.14	7.2	0.7
1%Pd/MSU-X	0.25	3.9	1.1
1%Pd/MCM-41	0.21	4.5	3.2

impregnation does not significantly affect the original structure, in agreement with the XRD results. Note that mesostructured catalysts have framework pore sizes in the range 3–5 nm, which are large enough to accommodate the starting reagent and the reaction products. Crocker et al. [29] reports that the critical dimension of phenyl acetylene, essentially determined by the thickness of the benzene ring, is 0.3 nm. It is therefore suggested that the apparent substrate size dependence (see below) arises from spatial requirements for reactant chemisorption both on the external surface sites and in the restricted internal region.

3.2. Characterisation of Pd catalysts

Table 2 provides the H_2 chemisorption data for the catalysts used in the semi-hydrogenation of phenyl acetylene and 1-phenyl-1-hexyne. The H/Pd ratio of 1%Pd/HMS catalyst is lower than the ratio found for the 1%Pd/MSU and 1%Pd/MCM-41 catalysts. The H/Pd ratio of 0.14, obtained for 1%Pd/HMS, suggests the presence of surfactant residues on the metallic sites of palladium. The surfactant coating of the Pd ensembles results in a significant decrease of the ability to chemisorb hydrogen. H_2 chemisorption generally takes place dissociatively, resulting in the formation of two non-stoichiometric bulk hydride phases coexisting below the critical temperature (300 °C). At low H_2 concentrations, the α -hydride phase is formed [30], which is a disordered solid solution almost identical in structure to the pure Pd lattice. At a high H_2 concentration, hydrogen-rich β -hydride phase is formed, which is an ordered interstitial solid solution exhibiting non-ideal behaviour [30].

TEM results for the Pd on HMS, MSU-X or MCM-41 catalysts revealed a very narrow palladium particle size distribution. The average values of the metal particle size obtained by TEM presented a lower value for 1%Pd/MSU-X and 1%Pd/HMS catalysts, indicating higher Pd dispersion for both catalysts. When TEM results are compared with chemisorption values, significant differences were observed for 1%Pd/HMS catalyst. This behaviour supports the presence of surface organic residues, resulting in a decreased ability to chemisorb hydrogen. The narrowest size distribution was observed for 1%Pd/HMS, with 85% of the particles ranging in size between 0.6 and 0.8 nm. Accordingly, the average particle diameters of 1%Pd/HMS and 1%Pd/MSU-X proved to be 0.7 and 1.1 nm, respectively (see Table 2).

On the other hand, a metal particle size in the range of 2–4 nm was observed for 1%Pd/MCM-41, including a large number of crystallites with mean particle diameter of 3.2 nm. One possible explanation for this behaviour could be that during the precursor reduction, the confinement inside the lower size channel

Table 3

Specific rate constant (k), turnover frequency (TOF) and selectivity to the styrene in the hydrogenation of phenyl acetylene at 298 K on Pd-supported catalysts

Catalysts	k ($\text{mol l}^{-1} \text{min}^{-1} \text{g}_{\text{cat}}^{-1}$) ^a	TOF ^a (s^{-1})	Selectivity to styrene ^b (%)
1%Pd/HMS	0.18	4	96
1%Pd/MSU-X	0.16	2	96
1%Pd/MCM-41	0.14	2	96

^a Conversion level 40%.

^b Conversion level 80%.

provides the Pd particles with more resistance to sinterisation under high temperature reduction and H_2 flow.

3.3. Phenyl acetylene semi-hydrogenation

The semi-hydrogenation of phenyl acetylene on Pd-supported catalysts was studied in tetrahydrofuran (THF) at a substrate:Pd ratio of 2500. To minimize mass transfer limitation, the catalysts were used as powdered samples with a small catalyst grain size (<200 μm) and the stirring was 1400 rpm. Pd catalyst activity and selectivity are related to high electron density and the rigidity of triple bond. This results in considerably stronger chemisorption than that of the corresponding of the double bond [24]. During the activity measurements performed in hydrogen, the alkyne concentration changed linearly over time. The calculated reaction rate was denoted k . The turnover frequencies (TOF), reported in Table 3, were determined from the rate constant normalised by the number of palladium sites, and the selectivity to styrene, calculated as the ratio of the styrene concentration over total products concentration at a total conversion of 80%, are reported in Table 3 for the palladium catalysts.

Fig. 4 compares the zero-order plots for different catalysts under identical reaction conditions. The linear decrease in the alkyne concentration over time was maintained up to a reaction time of 90 min for all of the Pd catalysts studied and a alkyne conversion of >90%, confirming that zero order kinetics applies (the initial rate of substrate hydrogenation corresponds to the reaction

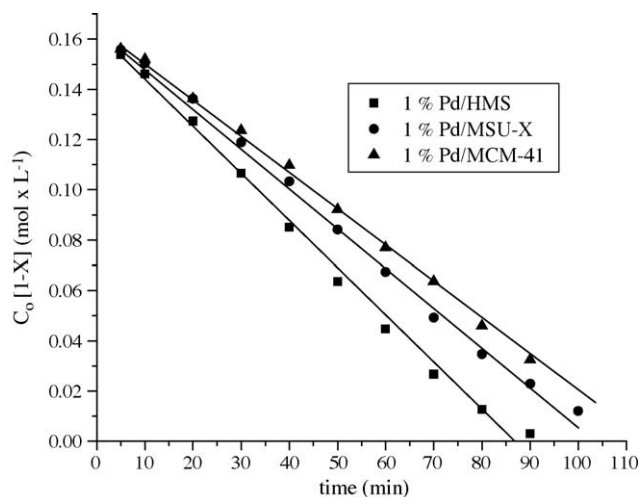


Fig. 4. Kinetic curve obtained for the phenyl acetylene hydrogenation on Pd-supported catalysts, $T = 298 \text{ K}$, $P_{H_2} = 1 \text{ bar}$, $R:P = 2500$ and THF as solvent.

rate). This behaviour is in agreement with previously reported results for phenyl acetylene hydrogenation over number of Pd-supported catalysts [7]. For the 1%Pd/HMS, the activity was slightly higher than that for 1%Pd/MSU-X and 1%Pd/MCM-41 catalysts (see Fig. 4), respectively. This result is not consistent with the difference in the Pd dispersions (see Table 2). This is indicative of a wormhole mesostructure silica effect because the interconnected channels can enhance the activity compared to catalysts having straight channels as possessed by the other studied supports. It can be readily seen that an increase in the Pd particle size of 1%Pd/MCM-41 and 1%Pd/MSU-X resulted in a decrease in the initial rate when comparing 1%Pd/HMS (see TEM values in Table 2), the most active sample, with a decline in the reaction rate that was observed for 1%Pd/MCM-41. Under the above conditions, 1%Pd/HMS, the catalyst with the smallest particle size, was the most efficient catalyst for the semi-hydrogenation of phenyl acetylene.

The results for the Pd-supported catalysts on mesostructured solids are presented in Table 3. The results indicate that the TOF for the 1%Pd/HMS catalyst is twice the values obtained for the other two Pd-supported catalysts under the same conditions. 1%Pd/HMS, the sample with the smallest particle size (see TEM results, Table 2) and mesoporous interconnected channels, was shown to be the most efficient catalysts for the semi-hydrogenation of phenyl acetylene. On other hand, the catalytic performances indicate that certain types of mesostructured solid can enhance catalytic activity.

On palladium-supported catalysts, the semi-hydrogenation of phenyl acetylene basically results in the predominant formation of styrene, which is attributed to the associative adsorption of the reactant and the consecutive addition of two adsorbed hydrogen atoms from below the axis of the triple bond [24]. All the catalysts studied demonstrated that high selectivity to styrene (96%) was achieved and remained constant even for the highest conversion degrees (see Fig. 5). Fig. 5 displays the evolution of the selectivity with respect to conversion level in the phenyl acetylene hydrogenation for a representative catalyst,

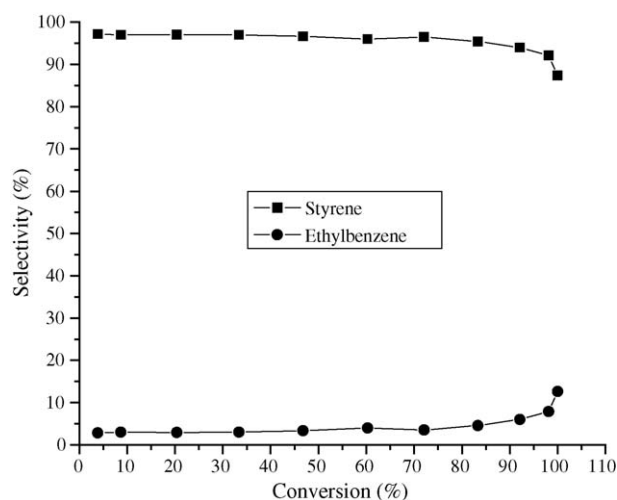


Fig. 5. Selectivity to hydrogenated products in the hydrogenation of phenyl acetylene over 1%Pd/HMS catalyst at 298 K, $P_{H_2} = 1$ bar and R:P = 2500.

indicating a predominant formation of styrene. Fig. 5 reveals that the over-hydrogenation product, ethyl benzene, was formed by simultaneous hydrogenation of the styrene molecule at high conversions. The trend was similar for all the studied systems.

The mode of adsorption over different mesostructured solids as supports is the only defining factor in the phenyl acetylene reactivity. Alkynes are known to have strong complexing abilities, and this is one of the reasons for the high semi-hydrogenation selectivity over Pd, the adsorbing alkyne prevents the re-adsorption of the product alkene and hence the consecutive hydrogen addition cannot take place [31–33]. A comparison of the selected data for styrene selectivity is also presented in Table 3. It should be mentioned that styrene selectivity is fairly constant, in the range 96–98%, and up to approximately 80% of conversion for all studied catalysts. At higher conversion, a decrease in the selectivity and a simultaneous increase in the saturated compound derivative are observed (see Fig. 5).

3.4. 1-Phenyl-1-hexyne semi-hydrogenation

For 1-phenyl-1-hexyne hydrogenation, the reaction rate (k), the turnover frequency (TOF), and the selectivity to *cis*-1-phenyl-1-hexene (defined as the ratio of *cis*-1-phenyl-1-hexene to all of the hydrogenated products) are compiled in Table 4 for the palladium catalysts. In contrast with the reaction of phenyl acetylene, marked differences in activity were observed between 1%Pd/HMS and 1%Pd/MSU-X, 1%Pd/MCM-41 catalysts. This implies that the pronounced initial activity of 1%Pd/HMS is characteristic of the small Pd particles and the mesoporous interconnected channels. The differences mainly reflected in the activity was even more drastic than that for the reaction of phenyl acetylene, and may be associated with the differences in the chemical structure and size of the phenyl acetylene and 1-phenyl-1-hexyne, while no appreciable difference was observed for selectivity.

The hydrogenation of 1-phenyl-1-hexyne was carried out at 298 K and 1 bar in THF. No catalyst deactivation during the catalytic run was observed.

The semi-hydrogenation of alkynes has been investigated on some Pd-supported catalysts [7,11–13,34]. Michalska et al. [35] reported 77 and 80% *cis*-alkene selectivity for hydrogenation of 1-phenyl-1-propyne and 1-phenyl-1-butyne, respectively, over palladium catalysts supported on heterocyclic polyamides. In previous experiments on phenyl alkyl acetylenes, a ~95% *cis*-alkenes selectivity was reported for the hydrogenation of different phenyl alkyl acetylenes on palladium catalysts sup-

Table 4
Specific rate constant (k), turnover frequency (TOF) and selectivity to the *cis*-isomer in the hydrogenation of 1-phenyl-1-hexyne at 298 K on Pd-supported catalyst

Catalysts	k ($\text{mol l}^{-1} \text{min}^{-1} \text{g}_{\text{cat}}^{-1}$)	TOF ($\times 10^3$) (s^{-1})	Selectivity to <i>cis</i> -isomer ^a (%)
1%Pd/HMS	0.27	60	79
1%Pd/MSU-X	0.10	11	79
1%Pd/MCM-41	0.11	6	83

^a Conversion level 50%.

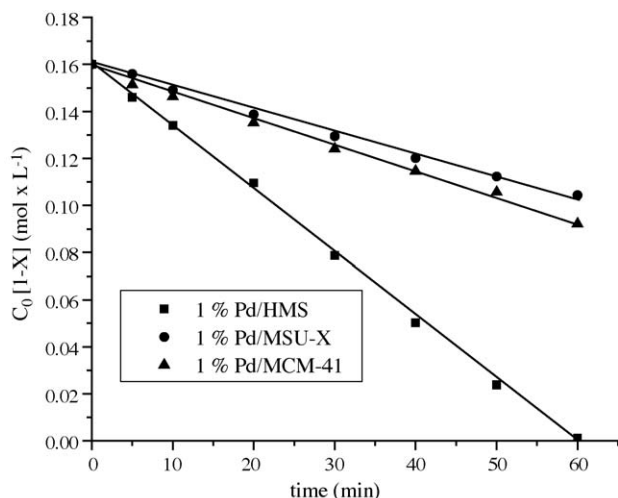


Fig. 6. Kinetic curve obtained for 1-phenyl-1-hexyne hydrogenation over Pd supported catalysts at 298 K, $P_{H_2} = 1$ bar and R:P = 2500.

ported on mesoporous and pillared clays materials with a linear trend for the conversion percentage versus reaction time [8,36]. Mesoporous solids, such as HMS and MSU-X, display a new advantage for the hydrogenation of phenyl alkynes with long alkyl chains as supports of palladium catalysts.

Fig. 6 displays the evolution of the alkyne concentration over time in the 1-phenyl-1-hexyne hydrogenation for all the studied catalysts. It can be seen that the conversion increases linearly with time indicating a zero order dependence on the concentration of the 1-phenyl-1-hexyne molecule. Even though the trend was similar for all the studied catalysts, significant differences in the catalytic activity were observed, where the 1%Pd/HMS catalyst was the most active. A summary of the results, expressed as zero-order specific rate constant and turnover frequency (TOF), for the three studied catalysts are provided in Table 4.

It is remarkable that the 1%Pd/HMS catalyst exhibits much higher activity in comparison with the other Pd-supported catalysts. The observed behaviour may be attributed to the wormhole framework effect and the high textural porosity since the presence of interconnected channels can enhance the activity compared with straight channels as observed in the others studied supports. This result is due to an increased possibility of reactant entrance in multiple locations. This trend is similar to the one observed in the phenyl acetylene hydrogenation, where Pd ensembles were partially destroyed by the presence of chemisorbed nitrogen compounds that had not been completely eliminated in the synthesis process, producing a significant drop in the H/Pd ratio. For 1%Pd/MSU-X and 1%Pd/MCM-41 catalysts, the turnover frequencies (TOF) and specific rate constant (k) (Table 4) do not display many differences, and they fall within the experimental error. The higher TOF values obtained for 1%Pd/HMS (see Table 4) were significantly higher in comparison to those exhibited by 1%Pd/MSU-X and 1%Pd/MCM-41 catalysts may also be partially related to the differences in the mesostructure support, which ensured an easier solvation of the reactant with THF due to interconnected channels, which is not observed in the other catalysts. This may be attributed

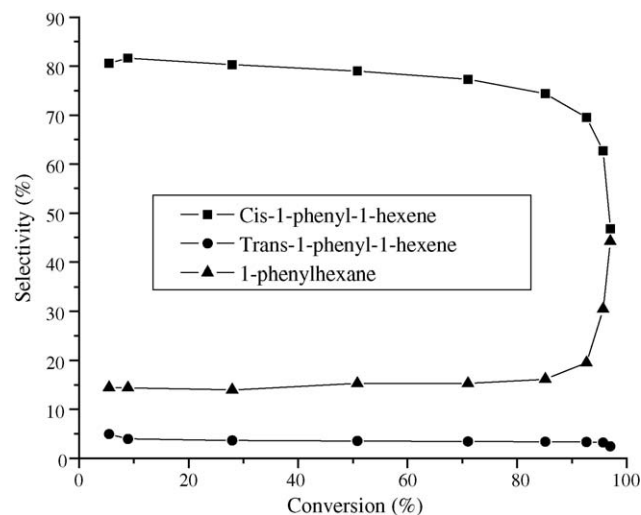


Fig. 7. Selectivity as a function of conversion for 1-phenyl-1-hexyne hydrogenation on 1%Pd/HMS catalyst at 298 K, $P_{H_2} = 1$ bar and R:P = 2500.

to several factors, including differences in the size particles. More importantly, the wormhole framework effect occurs when the structure contains interconnected channels. Furthermore, a larger alkyl chain limits the available space inside the channels, which may affect molecule mobility. Therefore, the probability for reaction with hydrogen is higher for the larger molecules, as is the case for 1-phenyl-1-hexyne. Additionally, it is worth mentioning that this effect is even more important in the mesoporous solids.

Fig. 7 shows the evolution of the selectivity during 1-phenyl-1-hexyne hydrogenation for a representative Pd-supported catalyst. The main product is the *cis*-1-phenyl-1-hexene with a low proportion of *trans*-1-phenyl-1-hexene and 1-phenylhexane, respectively. The selectivity to the *cis*-1-phenyl-1-hexene is fairly constant up to approximately 70% of conversion, when it starts to decrease. Simultaneously, an increase in both the *trans*-1-phenyl-1-hexene and the 1-phenylhexane derivative is observed. Similar behaviour was exhibited by the other catalysts with some differences in the selectivity levels. Table 4 summarises the selectivity for the different studied catalysts during the hydrogenation of the 1-phenyl-1-hexyne obtained at the same conversion level for the studied catalysts. The selectivity to the *cis*-isomers is in the range 80–83% for conversion levels 10 and 50% for all studied catalysts. As reported in the literature, *trans*-isomer is always formed in the alkyne hydrogenation, either as initial products or as a result of isomerisation of the *cis*-isomers [24]. It is generally accepted that direct *trans*-isomer formation may occur via the addition of molecular hydrogenation to the adsorbed alkyne molecule [37]. The problem of stereoselectivity has been rarely addressed in recent years and only a few papers have disclosed results on the hydrogenations of internal alkynes [7,35,38].

4. Conclusions

The obtained results show that, in general, the effect of the support on the catalytic performance of palladium-supported

catalysts is very important. The Pd supported on mesostructured solids are effective catalysts in the stereoselective hydrogenation of phenyl acetylene and 1-phenyl-1-hexyne in the liquid phase. The catalytic performance was different for each catalyst studied. The most efficient catalyst was 1%Pd/HMS in comparison to 1%Pd/MSU-X and 1%Pd/MCM-41 catalysts. This behaviour is attributed to the presence of interconnected wormhole channels in 1%Pd/HMS, which permits an increase in accessibility in comparison with the other studied supports. The catalytic activity is modified due to a mesostructured material effect and the preferential adsorption of phenyl alkynes molecules. The main hydrogenation product was the *cis*-1-phenyl-1-hexene and styrene, and over-hydrogenation to alkanes only appears at high conversion levels.

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