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Journal of Catalysis 220 (2003) 372–381
JOURNAL OF CATALYSIS
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Pd nanoparticles in hydrotalcite: mild and highly selective catalysts for alkyne semihydrogenation

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Received 17 March 2003; revised 3 June 2003; accepted 3 June 2003

Abstract

Pd nanoparticles incorporated in a hydrotalcite (HT) host were prepared via anion exchange between a dilute suspension of HT–nitrate and a Pd hydrosol stabilized by the anionic surfactant sodium dodecyl sulfate. Samples of two of the resulting Pd organoclays, Pd–HT1 and Pd–HT2, with metal contents of 0.1 and 0.42%, respectively, were subjected to further investigations. Characterization via ICP-AES, XRD, and TEM measurements indicated the deposition of fairly monodispersed Pd particles, predominantly on the external surface of the HT layers. The Pd–HT samples proved to be efficient catalysts for the liquid-phase semihydrogenations of both terminal and internal alkynes under mild conditions. For the transformation of phenylacetylene to styrene, a bond selectivity of 100% was obtained, and the *cis* stereoselectivities for the hydrogenations of the internal alkynes 4-octyne and 1-phenyl-1-pentyne reasonably approached 100%. The catalytic activity of Pd–HT increased with the Pd dispersion, whereas the alkene selectivity remained essentially unaffected.

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Keywords: Palladium; Hydrotalcite; Anionic surfactant; Hydrogenation; Phenylacetylene; 4-Octyne; 1-Phenyl-1-butyne; Selectivity

1. Introduction

Hydrotalcite-type (HT) anionic clays (also known as layered double hydroxides) are homogeneous, basic, mixed metal hydroxides with a lamellar structure. HT materials can be characterized by their chemical composition, basal spacing, and stacking sequence [1–3]. The general formula of HT is $M^{2+}_{1-x}M^{3+}_{x}(OH)_2(A^{n-})_{x/n} \cdot yH_2O$, where M^{2+} and M^{3+} are di- and trivalent metals, respectively, and A^{n-} is an interlayer anion ($CO_3{}^{2-}$, Cl^-, or $NO_3{}^-$) having a valence of n, which influences the basal spacing. The value of x is in the range 0.17–0.33 [2,4,5]. The structure of the HT compounds consists of brucite-like $Mg(OH)_2$ layers, in which the Mg^{2+} ions are surrounded by hydroxyl ions in an octahedral arrangement [1,6–8]. Isomorphous substitution of Mg^{2+} by Al^{3+} renders the brucite-type sheets positively charged; electric neutrality is maintained by inorganic anions of relatively high mobility, located in disordered interlayer regions containing water molecules [1–8]. One of the most important properties of HT-like compounds is the high anion-exchange capacity, related to their lamellar structure, which allows replacement of the original interlayer anions by others, including anionic surfactants [1,2,5,8–11].

In recent years, HT compounds have been extensively studied as anion exchangers [2,5,10,11], catalyst precursors, and catalysts [1,3,12]. Calcination of HTs at temperatures over 723 K results in thermal decomposition, leading to the formation of basic mixed oxides that have proved to be efficient catalysts for a variety of organic reactions, including aldol condensations [13–16], nitrile hydrogenation [17], phenol oxidation [18], and alkoxylation [19]. The application of HT as a support material for transition and noble metal catalysts has also been investigated [20–22]. Rh, Ru, Ir, Pd, and Pt-based catalysts have been prepared from HT-type anionic clays by coprecipitation, with a view to methane activation studies [23,24]. Pd/HT materials synthesized by a similar coprecipitation method have been examined as catalysts for selective hydrodechlorination reactions [25]. Further, HT-supported Pd catalysts prepared by impregnation have been employed for phenol hydrogenation [26]. Another synthetic method, based on the reduction of $PdCl_4{}^{2-}$ after anion exchange, leading to the formation of a Pd/HT

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0021-9517/$ – see front matter © 2003 Elsevier Inc. All rights reserved.
doi:10.1016/S0021-9517(03)00269-0

catalyst applied for C–C coupling reactions, was recently reported by Choudary et al. [27].

The synthetic utility of selective alkyne hydrogenations has long been established for the preparation of fine chemicals and biologically active compounds [28–30]. Although a number of catalytic applications for transition and noble metal–HT systems have been described, no published information is currently available on their potential use for alkyne semihydrogenations. The main objective in alkyne semihydrogenation is to achieve the highest alkene selectivity possible. As confirmed by previous studies, Pd is the most selective metal catalyst for the semihydrogenation of monosubstituted acetylenes, and also for the transformations of nonterminal alkynes to *cis*-alkenes [31–34]. The pronounced selectivity of Pd is attributed to stronger chemisorption of the alkyne species on the active center than that of the alkene, which is related to the high electron density and the restricted rotation of the C≡C bond [30,32,34]. In the present work, Pd–HT samples were prepared via a surfactant-mediated synthetic route in a micellar system. The hydrophobic Pd–HT materials were tested as catalysts in the liquid-phase semihydrogenations of phenylacetylene, 4-octyne, and 1-phenyl-1-pentyne.

2. Experimental

2.1. Materials

A HT compound with exchangeable NO_3^- gallery ions ($HTNO_3$) was synthesized by a standard method described earlier [35]. Aqueous solutions of $Al(NO_3)_3 \cdot 6H_2O$ and $Mg(NO_3)_2 \cdot 9H_2O$ (Mg:Al = 2:1) were added dropwise to a NaOH solution under a N_2 atmosphere during stirring, which was maintained at 333 K for 5 h. The pH of the reaction system was adjusted to between 9 and 10. When the reaction was completed, the white precipitate that had formed was aged in an aqueous solution at 333 K for 7 days. The product was purified by washing with distilled water in several centrifugation/redispersion cycles (Sorwall RC centrifuge, 3500 rpm). XRD analysis revealed the formation of a crystalline material $HTNO_3$ (the basal spacing d_L for the dry clay was 0.78 nm).

Pd hydrosols were prepared via reduction of the precursor palladium acetylacetonate ($Pd(acac)_2$, 99%, Aldrich) in the presence of the anionic surfactant sodium dodecyl sulfate (NaDS, 99%, Sigma). The precursor was first dissolved in chloroform (1% w/w) and then introduced into the aqueous surfactant solution (8 mM) so as to produce a normal micellar system (0.1 mM Pd) [36,37]. Reduction by a 50-fold excess of aqueous hydrazine (55% w/w) afforded surfactant-stabilized Pd nanoparticles. On addition of the NaDS-stabilized Pd hydrosol to an aqueous suspension of $HTNO_3$ (2% w/w), anion exchange of NO_3^- by DS^- occurred, resulting in the formation of a hydrophobic clay organocomplex. Simultaneously, the bare Pd particles released were deposited on the clay lamellae. After removal of the excess surfactants in ethanol by centrifugation/redispersion sequences, the Pd–HT material was dried in vacuum at 353 K. Variation of the Pd hydrosol:HT suspension volume ratio afforded Pd–HT materials with different Pd contents.

For comparative investigations, 5% Pd on γ-Al_2O_3 (Pd/Al_2O_3, a Merck product) and 5% Pd on activated carbon (Pd/C, a Janssen product) were utilized. The Pd dispersions D of the samples were determined from TEM measurements as $D = 0.885/d$, where d is the mean particle diameter (nm) [38]. The dispersion values obtained were 0.47 and 0.17 for Pd/Al_2O_3 and Pd/C, respectively.

2.2. Methods

X-ray diffraction (XRD) measurements were made in the scattering angle range $1^\circ \leqslant 2\Theta \leqslant 20^\circ$ with a Philips PW diffractometer at 40 kV and 35 mA (Cu-K_α radiation, $\lambda = 0.154$ nm). Wet samples were taken from the sediments of the suspensions formed in different solvents. In order to prevent solvent evaporation, the sample holder was covered with a Mylar film. The d_L values were calculated from the first-order (001) Bragg reflections by using the PW 1877 powder diffraction software.

The Pd contents of the samples were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES), with a Jobin Yvon 24 sequential ICP-AES spectrometer at 229.7 and 324.3 nm. Before measurement, the Pd–HT samples were dissolved in aqua regia. The Pd contents were obtained from the emission intensities by means of a calibration curve.

The particle-size distributions were obtained from transmission electron microscopy (TEM) images, taken with a Philips C-10 electron microscope, with a LaB_6 cathode at 100 kV. The instrument was equipped with a Megaview II digital camera. The samples were suspended in hexane and mounted on a plastic film supported on a Cu grid. The mean particle diameters d were calculated as $\sum n_i d_i / \sum n_i$ ($\sum n_i > 250$), by using the UTHSCSA Image Tool program.

The total organic carbon (TOC) contents of the samples were determined with a Euroglass TOC 1200 apparatus at 309 K.

Na^+ analysis was carried out by using a Jenway PFP 7 flame photometer. Prior to measurement, the samples were dissolved in 5 cm^3 of cc HCl, followed by addition of the same amount of distilled water. Na^+ contents were gained by means of a calibration curve constructed from the results on NaCl solutions of known concentrations (0–10 ppm). The intensities observed for the solutions of the Pd–HT samples were corrected for the intensity of a blank solution containing a 1:1 mixture of cc HCl and distilled water.

The catalytic test reactions were performed in an automated liquid-phase reactor, illustrated in Fig. 1. The reactants phenylacetylene, 4-octyne, and 1-phenyl-1-pentyne, all Aldrich products of 99% purity, were used as received.

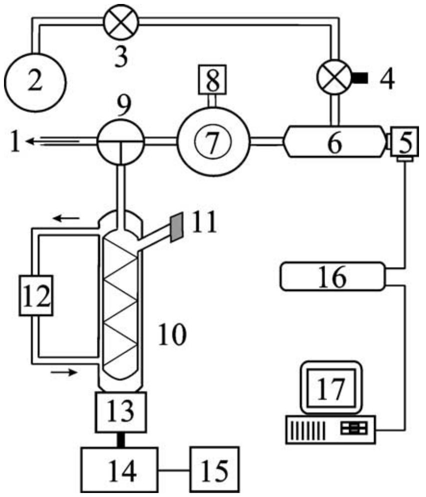

Fig. 1. Experimental apparatus for catalytic hydrogenation reactions: (1) vacuum piping, (2) hydrogen reservoir, (3) two-way valve, (4) metering valve, (5) pressure transmitter, (6) high-pressure hydrogen chamber, (7) pressure regulator, (8) pressure gauge, (9) three-way valve, (10) reaction vessel, (11) septum, (12) thermostat, (13) rubber cup, (14) DC motor, (15) variable-speed motor controller, (16) pressure transmitter interface, and (17) PC.

Before measurements, the solvents toluene, tetrahydrofuran (THF), ethanol, and hexane were dried and distilled under a N_2 atmosphere.

Measurements were carried out with 10 mg of Pd–HT in a glass reaction vessel at 298 K. After evacuation and flushing with H_2, the catalyst was pretreated in 10^5 Pa of static H_2 for 1 h. Next, 1 cm^3 of solvent was added, and vigorous stirring was applied for 45 min. The reaction was subsequently initiated by injecting the alkyne substrate into the reaction vessel. Hydrogenation was conducted under efficient stirring (1400 rpm) to eliminate diffusion control. The H_2 consumption was balanced by a pressure regulator at the expense of the high-pressure side; accordingly, a constant pressure of 10^5 Pa was maintained throughout the reaction. The H_2 chamber was connected to a pressure transmitter, interfaced to a PC. The H_2 uptake was recorded continuously at a data collection frequency of 0.5 s^{-1}. After the reaction was completed, the catalyst was removed by gravity filtration. Quantitative analysis of the products was performed with an HP 5890 gas chromatograph equipped with a DB-5 capillary column and a flame ionization detector (FID). The S:Pd values were expressed as [mole reactant]:[mole Pd]. The catalytic activity was characterized by the turnover frequency (TOF), calculated from the initial reaction rate R (cm^3 H_2 min^{-1} $g\,Pd^{-1}$) as $\mathrm{TOF} = 7.253 \times 10^{-5}\ R/D$, where D is the dispersion of Pd, obtained from TEM measurements, as noted above [38].

Reusability of the samples was investigated in repeated catalytic reactions. It was found that neither the catalytic activities nor the selectivities decreased appreciably in up to 3 runs. The conversion curves could be reproduced within ±2.5% in repeated runs, and the changes in the selectivities of the main reaction products were within the range of experimental error in the GC analysis (±0.1–0.28%). It follows that no Pd leaching of the samples occurred during catalytic applications.

3. Results and discussion

The synthesis of Pd particles is based on the application of the anionic surfactant NaDS, which increases the solubility of $Pd(acac)_2$ and chloroform in water through a solubilization effect [39], thereby producing an aqueous micellar solution of $Pd(acac)_2$, previously dissolved in chloroform. The hydrophobic alkyl chains of the surfactant molecules are directed to the inner pool containing the precursor molecules, whereas the hydrophilic head groups are situated on the outer shell of the swollen micelles, in contact with the aqueous phase. Addition of an aqueous hydrazine solution to this micellar system resulted in the formation of Pd nanoparticles in the form of a highly stable hydrosol, stabilized both sterically and electrostatically by the surfactant molecules: the hydrophobic parts of the NaDS molecules were adsorbed in a perpendicular orientation on the surface of the Pd nanoclusters and further aggregation was therefore prevented by a dense, protective surfactant layer around the metal particles [40]. The proposed mechanism for the interaction of the Pd hydrosol with the anionic clay lattice is outlined in Fig. 2.

On addition of an aqueous $HTNO_3$ suspension to the Pd hydrosol stabilized by NaDS, an ion-exchange reaction took place between the DS^- and the $NO_3{}^-$, which released the Pd nanoparticles and made the HT surface hydrophobic. After complete decomposition of the surrounding protective surfactant layer, the Pd particles were adsorbed on the surface of the clay lamellae. In this way, a hydrophobic Pd organoclay was formed, which, unlike hydrophilic clays, is capable of

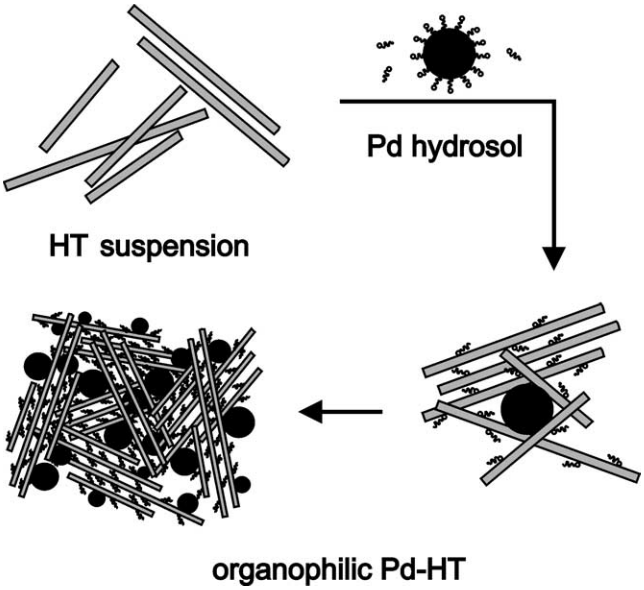

Fig. 2. Schematic representation of Pd–HT formation via anion exchange.

Table 1
Characterization of organophilic Pd–hydrotalcite catalysts

Sample	Pd (%)	d_L (nm)	d (nm)	D
	ICP-AES	XRD	TEM	
Pd–HT1	0.10	2.73	2.4	0.37
Pd–HT2	0.42	2.77	3.5	0.25

swelling in the organic solvents usually applied as dispersion media in liquid-phase catalytic reactions [41,42].

For further investigations, two representative Pd–HT samples with low Pd loadings were selected, Pd–HT1 and Pd–HT2, for which the Pd contents determined from ICP-AES were 0.10 and 0.42%, respectively.

TOC analysis revealed that the anion-exchange capacity of the pristine HT material treated with the same surfactant solution (1.77 meq g^{-1}) did not exhibit any significant difference from those of the Pd organoclays. It follows that the Pd–HT samples contain surfactant molecules fixed by electrostatic interactions only in the anion-exchange positions of the clay lattice, and thus the presence of residual NaDS on the surface of the Pd particles may be excluded. This finding complies with the results of Na^+ analysis: the Na^+ contents of the samples proved to be 0.0062 and 0.0084% for Pd–HT1 and Pd–HT2, respectively. As Na^+ ions originate only from NaDS, it may safely be assumed that the effect of residual surfactant molecules on the Pd particles is negligible. Further, Na^+ is unlikely to have an electronic effect on the Pd particles.

Characteristic data on the Pd–HT samples are collected in Table 1.

The TEM micrographs of the Pd–HTs revealed the appearance of quasispherical Pd particles with relatively narrow size distributions (Fig. 3). For Pd–HT1, 74% of the Pd crystallites had diameters less than 3 nm and only few particles measuring over 4 nm were observed. For Pd–HT2, the size distribution was broader and the overall crystallite dimensions were larger. As compared with Pd–HT1, a significant decline in the number of particles measuring 1–2 nm was found, whereas the frequency of crystallites 3–6 nm in size was increased considerably. Nevertheless, aggregates larger than 6 nm were not detected and therefore no appreciable increase in the mean particle diameter could be established, as shown in Table 1. It follows that the Pd particles may be considered fairly monodispersed for both samples, which confirms the stabilizing effect of the surfactant molecules in the hydrosol and the absence of surface aggregation after Pd deposition.

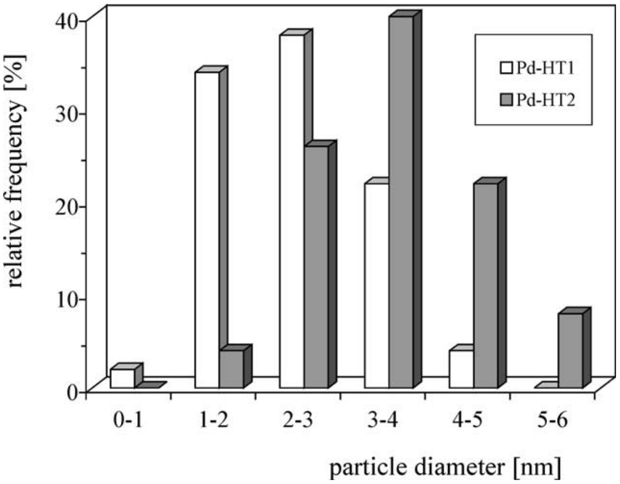

Fig. 3. Particle-size distributions of Pd–HT1 and Pd–HT2.

The pronounced d_{001} reflections observed for the Pd–HTs by means of XRD measurements confirmed that the lamellar structure of the HT host was preserved after the incorporation of the Pd particles. The basal spacings of the Pd–HTs (see Table 1) were somewhat higher than that of the corresponding organoclay in the absence of Pd particles (2.52 nm), which points to the presence of Pd nanoparticles in the interlayer region of the HT host. This is supported by a slight broadening of the characteristic d_{001} reflections, indicating a less ordered structure for the Pd–HTs than that of the pristine HT material. However, regular intercalation of the Pd particles between the clay sheets is rather unlikely. It follows that, in accordance with the TEM images, a substantial proportion of the Pd particles are situated on the external surface sites of the HT lamellae.

The semihydrogenation of phenylacetylene has been investigated on various supported Pd catalysts [43–46] and on clay-intercalated Pd crystallites [47]. For Pd supported on pumice, high turnover frequencies and a selectivity of 80% for the formation of styrene have been reported [45]. For Pd on vitreous supports, a 100% selectivity for styrene production and a linear trend for the percentage of styrene vs time have been described [46].

The transformation of phenylacetylene on Pd–HT1 was studied in toluene, at S:Pd = 2500. The results are displayed in Fig. 4.

The marked initial activity of Pd–HT1 gradually diminished as the hydrogenation proceeded, and complete con-

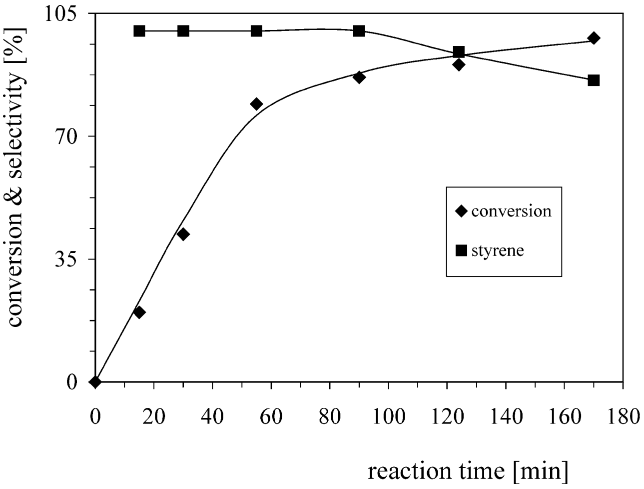

Fig. 4. Transformation of phenylacetylene on Pd–HT1: $m = 10^{-3}$ g, $T = 298$ K, $p = 10^5$ Pa, S:Pd = 2500.

version was attained at a reaction time of 170 min. The selectivity of styrene formation proved to be 100% up to 90 min; overhydrogenation, leading to the appearance of 6% of ethylbenzene in the product mixture, was first observed at 124 min. Hence, in order to produce only one semihydrogenated product with a high conversion (87%), the reaction should be terminated at a reaction time of 90 min.

For the above reaction investigated on Pd–HT2 under the same conditions (Fig. 5), the conversion was substantially lower than that observed on Pd–HT1, which is consistent with the difference in the Pd dispersions (0.37 and 0.25 for Pd–HT1 and Pd–HT2, respectively). This is indicative of a decrease in the number of active sites for Pd–HT2, which may be related to the appearance of Pd particles larger than 4 nm. In fact, the latter particles mainly consist of crystal planes (terrace atoms with high coordination number), whereas small particles, such as those predominant in Pd–HT1 (see Fig. 3) mostly contain Pd atoms with low coordination numbers (edge or corner atoms) that are more active in hydrogenation. It follows that a site modification effect may account for the substantial activity difference observed for the Pd–HTs, which is in accordance with previous studies disclosing that alkyne hydrogenation is a structure-sensitive reaction at medium to high Pd dispersions [34,48,49].

On decrease of the S:Pd ratio from 2500 to 700, an appreciable increase in the conversion of phenylacetylene on Pd–HT2 could be achieved (Fig. 5). The 100% selectivity of styrene formation throughout the reactions in both cases is related to the conversions being substantially lower than the 87% obtained for Pd–HT1, above which ethylbenzene formation was observed.

The evidence that the conversion plots were saturation curves for both Pd–HTs indicated that these samples differed from the conventional supported Pd catalysts cited above. This points to the existence of Pd crystallites in the interlamellar regions of HT, which may participate in the reaction, in addition to those situated on the external surface of the clay lamellae. Access to such internal active sites can be achieved through diffusion of the reactant molecules between the layers, which tends to have a limiting effect on the reaction rate. On the incorporation of the Pd particles into the organophilic HT host, the interlayer distance increased from 1.74 to 1.97 ± 0.2 nm (see Table 1). This implies that particles smaller than 2 nm are most likely to be intercalated between the clay lamellae. As revealed by Fig. 3, such particles are more abundant in Pd–HT1, which may therefore contain a larger amount of interlamellar Pd particles than Pd–HT2. Accessibility for the reactants to these species is suggested by the pronounced catalytic activity of Pd–HT1, which may also account for the moderate overhydrogenation observed at high conversions. Nevertheless, direct alkane production may be ruled out for both samples [32,50]. In fact, both catalysts displayed an excellent selectivity for styrene formation, which considerably exceeded that reported for the same reaction conducted on Pd nanoparticles intercalated in a hydrophilic clay host [47].

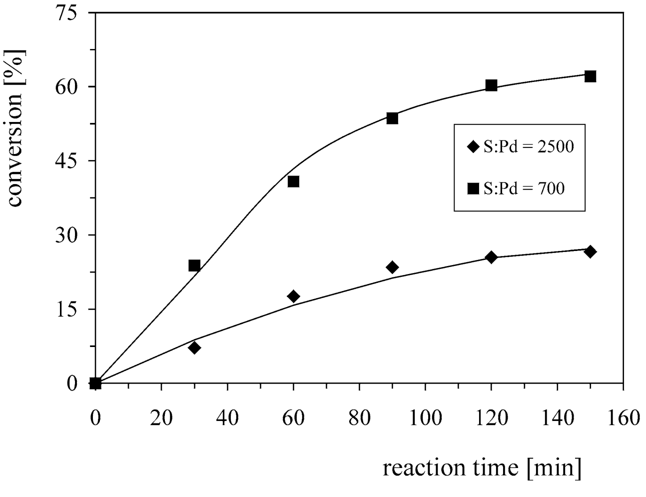

Fig. 5. Transformation of phenylacetylene on Pd–HT2: $m = 10^{-3}$ g, $T = 298$ K, $p = 10^5$ Pa.

In liquid-phase reactions in organic solvents, the hydrophobic character of the Pd–HT samples is a distinct advantage as compared with catalysts prepared from hydrophilic clay hosts, which tend to be ill-dispersed in most organic media. Moreover, depending on the solvent employed for the reaction, the catalytic properties of the Pd–HTs may be influenced by the swelling ability of the HT host, especially when interlamellar Pd particles are regarded as potential active centers. In order to gain more information on the role of the dispersion medium for the above reaction, the catalytic performance of Pd–HT1, the sample with higher activity, was studied in different solvents. The results are listed in Table 2.

For the solvents toluene, THF, and ethanol, no important difference in the turnover frequency was observed, and the conversions did not vary to any appreciable extent. On the other hand, when hexane was applied, significant decreases in both the initial rate and the conversion were experienced. The question arises whether the change in the catalytic activity of Pd–HT1 is related to the variation in H_2 solubility in the above dispersion media. The corresponding data in Table 2, taken from the literature, reveal that the solubilities of H_2 in both toluene and THF are very close and higher

Table 2
Effect of the solvent on the hydrogenation of phenylacetylene on Pd–HT1

Solvent	R[a] (cm^3 H$_2$ min^{-1} g^{-1} Pd)	TOF (s^{-1})	Conversion[b] (%)	S_{styrene}[b] (%)	δ[c]	d_L[d] (nm)
Toluene	8264	1.62	79.2	100	3.4	3.48
THF	7817	1.53	68.9	100	3.5	3.62
Ethanol	7623	1.49	70.2	100	2.9	3.12
Hexane	5612	1.10	56.7	100	4.7	2.80

[a] $m = 10^{-3}$ g, $T = 298$ K, $p = 10^5$ Pa, S:Pd = 2500.
[b] Reaction time: 55 min.
[c] Solubility of H_2 (10^3 mol dm^{-3}), taken from Ref. [52].
[d] Basal spacing, obtained from XRD measurements.

than that in ethanol [51–53]. Further, the highest H_2 solubility (4.7 mmol dm^{-3}) has been reported for hexane [51–53]. This trend, however, does not conform with our results, indicating the lowest activity in hexane. Accordingly, no systematic correlation can be discerned between the H_2 solubility and the catalytic performance of Pd–HT1. This finding is consistent with the results of earlier studies on the liquid-phase hydrogenation of cyclohexene: whereas the TOF values over supported Pt and Rh particles varied considerably with the H_2 solubility, no such effect was found for Pd crystallites [54]. The absence of a solvent effect, based on H_2 solubility, may be regarded as an intrinsic feature of Pd, and, as suggested by Boudart, may be attributed to gas phase, liquid phase, and adsorbed H_2 being quasi-equilibrated in the reaction system [52,55]. Under such conditions, the surface coverage of hydrogen is claimed to be independent of the liquid-phase H_2 concentration [52].

On the other hand, the variation in d_L (Table 2) implies that the swelling ability of the catalyst depends on the solvent. In hexane, practically no swelling took place, as the value of d_L hardly surpassed that for the dry sample. In contrast, a similar substantial swelling was observed for toluene and THF, and a moderate swelling for ethanol. It is therefore reasonable to suggest that the catalytic activity of Pd–HT1 correlates with the swelling of the HT host, accompanied by disaggregation [56]; in a suitable solvent, this makes the interlayer active sites more readily accessible for reactant molecules. This may occur in toluene, THF, and even ethanol, for which the catalytic performance of Pd–HT1 was comparable with those in the former solvents. Thus, it may be stated that $d_L = 3.12$ nm, observed in ethanol, is sufficiently high to provide access for the reactant molecules to interlamellar Pd particles that may participate in hydrogenation, in addition to those available on the external surface sites of the HT host. As may be seen in Table 2, a further increase in the basal spacing has no significant effect on the TOF values. On the other hand, the lack of swelling in hexane suggests that the HT lamella packages are situated close together and hence access for the reactant molecules to the interlayer Pd crystallites tends to be restricted. This may account for the decreased activity of Pd–HT1, as related to diffusion limitations [52,56]. Nevertheless, the occurrence of interlamellar hydrogenation in hexane cannot be excluded with certainty.

The evidence that the TOF value observed in toluene slightly surpassed that in THF, despite the value of d_L being somewhat higher in the latter solvent, may be related to the reaction proceeding in a liquid mixture. It may be assumed that the adsorption of phenylacetylene from toluene is preferred to that from THF, thereby leading to an increased reactant concentration on the active sites, which may account for a higher catalytic activity. Moreover, the effect of solvent polarity on the reaction mechanism can also be taken into consideration. Since the polarity of phenylacetylene is similar to that of toluene (both being substituted aromatics), whereas THF is a more polar solvent, solvation of the reactant (or that of the activated complex) may be favored in toluene, which tends to contribute to an improved catalytic performance.

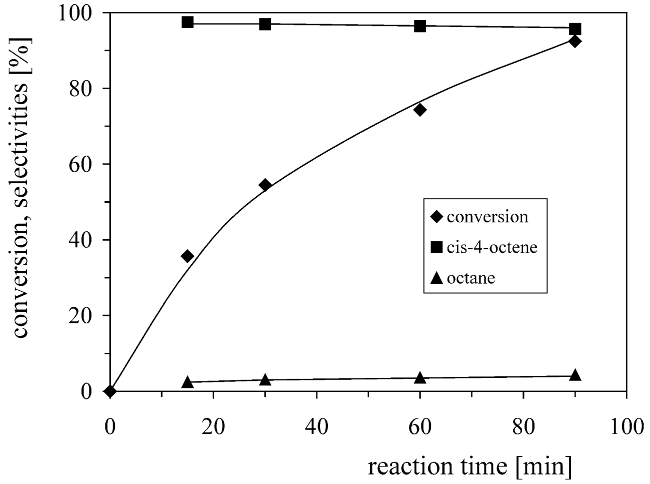

Fig. 6. Transformation of 4-octyne on Pd–HT1: $m = 10^{-3}$ g, $T = 298$ K, $p = 10^5$ Pa, S:Pd = 2500.

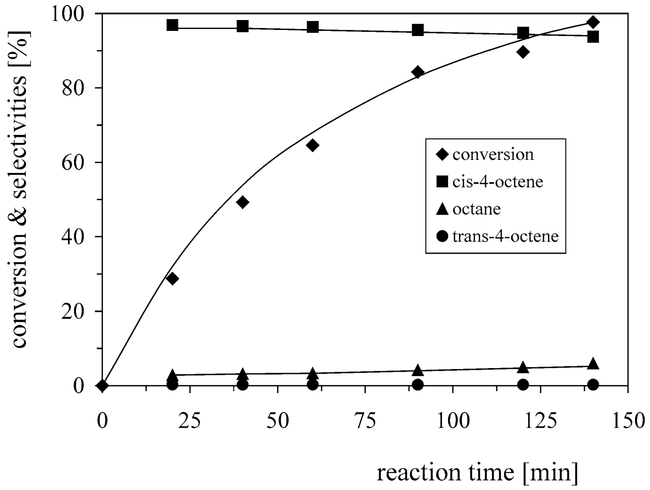

Fig. 7. Transformation of 4-octyne on Pd–HT2: $m = 10^{-3}$ g, $T = 298$ K, $p = 10^5$ Pa, S:Pd = 700.

It should be stressed that the moderate solvent effect observed for Pd–HT1 is merely reflected in the catalytic activities, as the selectivity of styrene formation proved to be the same in all solvents investigated.

The second reactant studied on the Pd–HTs was the internal alkyne 4-octyne, for which semihydrogenation resulted in the predominant formation of *cis*-4-octene (Figs. 6 and 7). It is generally accepted that the *cis* product is formed by the consecutive addition of two adsorbed hydrogens from below the axis of the triple bond [31,32]. For the transformation of 4-octyne on Pd–HT1, a conversion of 93% was obtained in a reaction time of 90 min. It was noteworthy that the initial stereoselectivity for *cis*-alkene formation was 97.5%, which had decreased merely to 95.6% by 90 min. Fig. 6 reveals that the overhydrogenation product octane was formed via simultaneous hydrogenation of both the reac-

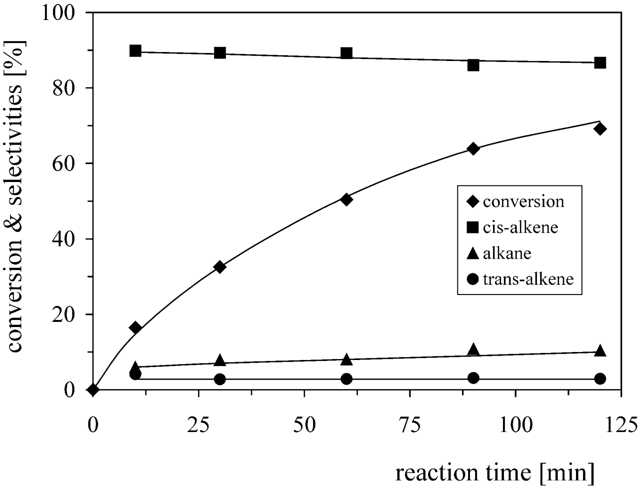

Fig. 8. Transformation of 1-phenyl-1-pentyne on Pd–HT1: $m = 10^{-3}$ g, $T = 298$ K, $p = 10^5$ Pa, S:Pd = 2500.

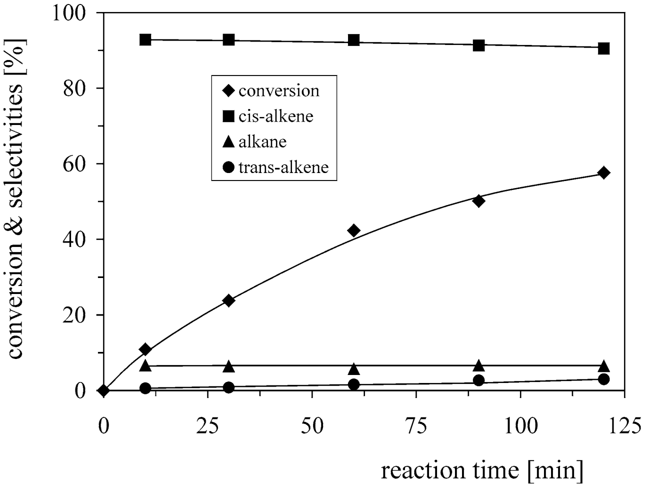

Fig. 9. Transformation of 1-phenyl-1-pentyne on Pd–HT2: $m = 10^{-3}$ g, $T = 298$ K, $p = 10^5$ Pa, S:Pd = 700.

Table 3
Hydrogenations of alkynes on Pd–HT catalysts

Catalyst	Reactant	R (cm^3 H$_2$ min^{-1} g^{-1} Pd)	TOF (s^{-1})	S[c] (%)	Y[d]
Pd–HT1[a]	Phenylacetylene	8264	1.62	100	–
Pd–HT2[b]	Phenylacetylene	4722	1.37	100	–
Pd–HT1[a]	4-Octyne	10559	2.07	96.8	1
Pd–HT2[b]	4-Octyne	5791	1.68	96.6	0.997
Pd–HT1[a]	1-Phenyl-1-pentyne	2296	0.45	89.2	0.969
Pd–HT2[b]	1-Phenyl-1-pentyne	1241	0.36	91.3	0.971

[a] $m = 10$ mg, $T = 298$ K, $p = 10^5$ Pa, solvent: 1 cm^3 of toluene, S:Pd = 2500.

[b] $m = 10$ mg, $T = 298$ K, $p = 10^5$ Pa, solvent: 1 cm^3 of toluene, S:Pd = 700.

[c] Selectivity of the main reaction product (alkene or *cis*-alkene), determined at a conversion of 50%.

[d] $Y = S_{cis}/S_{(cis+trans)}$, calculated from the selectivities at a conversion of 50%.

tant and the *cis*-alkene molecules [32]. It is important to stress that no *trans*-4-octene formation was detected at all, which is rather exceptional for the transformations of disubstituted acetylenes [32,46,57]. For the same reaction on Pd–HT2, similar observations were made: at a lower S:Pd ratio of 700 (see Figs. 6 and 7), both the conversion and the selectivities were comparable to those obtained on Pd–HT1. Full conversion of 4-octyne was achieved by a reaction time of 140 min. Likewise, only a minor decrease in the initial stereoselectivity of formation of the main product (97%) was experienced, in parallel with a similar increase in the selectivity of octane production. The stereoselectivity of *trans*-4-octene formation was negligible, as it never surpassed 0.3%. The unusually low extent of overhydrogenation observed for both catalysts can clearly be attributed to the triple bond of the reactant being more strongly adsorbed (due to its more electron-rich character) than the corresponding double bond. Accordingly, as long as the reactant 4-octyne is present, it displaces the *cis*-alkene from the active site, thereby preventing its readsorption, which would lead to overhydrogenation. In view of this “poisoning” effect of 4-octyne, the exceptionally high bond selectivity of the Pd–HTs is mainly thermodynamically controlled. However, the lack of *trans*-alkene formation may be related to a kinetic factor. As reported earlier, the two effects are frequently combined and cannot be readily distinguished [58].

For the sake of comparison, and with consideration of our previous experiments on higher aromatic alkynes [37,41], the catalytic performances of the Pd–HTs were further examined for the semihydrogenation of 1-phenyl-1-pentyne (Figs. 8 and 9).

As demonstrated by Figs. 8 and 9, the catalytic activities of the Pd–HTs in the case of 1-phenyl-1-pentyne were inferior to those observed for the hydrogenations of phenylacetylene and 4-octyne. By a reaction time of 120 min, the reaction rate had decreased considerably: the conversions obtained for Pd–HT1 and Pd–HT2 were 69.2 and 57.6%, respectively. Further, loss of the initial stereoselectivity for *cis*-alkene formation occurred to a lesser extent for Pd–HT2, for which the *cis* stereoselectivity at 10 min was higher (92.8%) than that for Pd–HT1 (89.9%). Both the overhydrogenation and the *trans* isomerization were found to be more pronounced on Pd–HT1. For the latter, overhydrogenation of both the reactant and the *cis*-alkene stereoisomer took place. The finding that the stereoselectivity of *trans*-alkene formation remained constant (2.9%) throughout the entire reaction time interval indicated that the *trans* stereoisomer was an initial product in the reaction [32,50,59]. On the other hand, on Pd–HT2, 1-phenyl-*trans*-1-pentene was formed via isomerization of the *cis*-alkene stereoisomer [50,60,61] and 1-phenylpentane was produced through overhydrogenation of the reactant.

Comparative data on the transformations of all reactants investigated on these Pd–HTs are presented in Table 3.

It may be seen that the initial rates determined for Pd–HT1 were considerably higher than those for Pd–HT2, which confirmed that, despite the marked difference in the S:Pd ratios, the catalytic activity of Pd–HT1 surpassed that of Pd–HT2 for all reactants. This activity difference is also reflected in the TOF values. On the other hand, little or no variation was experienced in the selectivities of the Pd–HTs at the same conversion level, and thus the Y values for the internal alkynes were nearly the same. It follows that, in contrast with previous observations in the literature, the selectivity of Pd–HT was not decreased by increasing the Pd dispersion [34,46,49]. This finding, however, is not unusual, as the lack of any particle-size effect on the selectivity has also been reported [49,62]. In our case, increase of the Pd dispersion mainly resulted in an enhanced catalytic activity, as found for Pd–HT1, which is therefore regarded as a more efficient catalyst than Pd–HT2.

As revealed by Table 3, the catalytic performances of the Pd–HT samples were also affected by the reactivity and size of the substrate molecules. It is generally suggested that terminal alkynes hydrogenate faster than internal ones, although, depending on the nature of the substituents, exceptions may occur [30,63]. In the current study, the activities for the hydrogenation of the terminal aromatic alkyne phenylacetylene proved to be lower than those for the internal aliphatic alkyne 4-octyne, although there was no substantial difference in the TOF values. It may be assumed that the hindering effect of the bulky aromatic ring on the chemisorption of the alkyne species was comparable to that of the long carbon chain of 4-octyne. On the other hand, a pronounced fall in the catalytic activities of both Pd–HTs, indicated by a severalfold decrease in the TOF values, was established for the hydrogenation of the bulkiest reactant, the internal aromatic alkyne 1-phenyl-1-pentyne, which suggests rather limited access of this reactant to the active sites. Nevertheless, a molecular sieving effect of the Pd–HTs may be excluded, in part because of the presence of Pd particles on the external surface of the HT host. Furthermore, each substrate is sufficiently small, at least in one dimension, to enter the solvated toluene interlayers. (The critical dimension of phenylacetylene, essentially determined by the thickness of the benzene ring, is 0.3 nm [64] and the extent of swelling for Pd–HT1 in toluene, relative to the dry state, is $\Delta = 0.75$ nm, obtained from the corresponding d_L values (see Tables 1 and 2).) 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. At any rate, the organophilic character of the HT material ensures that the interlayer spacings of the solvated Pd–HTs are large enough to accommodate each substrate, except when hexane was applied as a solvent, in which the extent of swelling was merely $\Delta = 0.07$ nm. Accordingly, no catalytic discrimination can be made between our reactants on the basis of their size and shape [65].

For further comparison, the catalytic performances of supported Pd catalysts (Pd/Al_2O_3 and Pd/C) were investigated for the same reactions. The results are displayed in Table 4.

Table 4
Hydrogenations of alkynes on supported Pd catalysts

Catalyst[a]	Reactant	R (cm^3 H$_2$ min^{-1} g^{-1} Pd)	TOF (s^{-1})	S[b] (%)	Y[c]
Pd/Al_2O_3	Phenylacetylene	5486	0.85	100	–
Pd/C	Phenylacetylene	5258	2.24	100	–
Pd/Al_2O_3	4-Octyne	11172	1.72	91.3	0.985
Pd/C	4-Octyne	9996	4.26	90.7	0.983
Pd/Al_2O_3	1-Phenyl-1-pentyne	7272	1.12	83.2	0.958
Pd/C	1-Phenyl-1-pentyne	10257	4.37	80.5	0.957

[a] $m = 10$ mg, $T = 298$ K, $p = 10^5$ Pa, solvent: 1 cm^3 of toluene, S:Pd = 250.

[b] Selectivity of the main reaction product (alkene or *cis*-alkene), determined at a conversion of 50%.

[c] $Y = S_{cis}/S_{(cis+trans)}$, calculated from the selectivities at a conversion of 50%.

The evidence that the TOF values obtained for Pd/C were significantly higher for each reaction than those for Pd/Al_2O_3 may be related in part to the organophilic character of the carbon support, which ensured a more facile dispersion of this sample in toluene than that of Pd/Al_2O_3. For the transformation of phenylacetylene, the catalytic activities of the supported Pd samples proved to be similar to those of the Pd–HTs. Although the TOF value obtained for Pd/C exceeded those for the Pd–HT catalysts, none of the differences were substantial. The selectivity of styrene formation was 100% for each sample. For the semihydrogenation of 4-octyne, the catalytic activities of the Pd–HTs were of a similar order to that of Pd/Al_2O_3, whereas the TOF value for Pd/C was considerably higher. On the other hand, the stereoselectivities of *cis*-alkene formation observed for the supported catalysts proved to be lower than those for the Pd–HT samples. For the transformation of 1-phenyl-1-pentyne, similar observations were made, the differences between the *cis* stereoselectivities of the Pd–HTs and those of the supported samples being even more pronounced. The evidence that the catalytic activities of both supported Pd samples surpassed those of the Pd–HTs is in accordance with our previous findings concerning a limited access for 1-phenyl-1-pentyne to the active sites of the Pd–HTs, including those in the interlamellar region. It may be concluded that, even at a low S:Pd ratio of 250, the catalytic activities of the supported Pd catalysts were not substantially higher than those of the Pd–HT samples, except for the reaction of 1-phenyl-1-pentyne. Moreover, for the transformations of internal alkynes, the Pd–HTs proved to be more stereoselective catalysts.

It is worth mentioning that, for the semihydrogenation of 1-phenyl-1-pentyne, the catalytic activities of the Pd–HT samples proved to be somewhat lower than those of low-loaded Pd-alkylammonium montmorillonites [41]. This may be attributed to several factors, including minor differences in the size distributions of the surface Pd crystallites. More importantly, the disaggregation of solvated HT materials occurs less readily than that of montmorillonite. Further, a higher alkyl chain packing density between the HT layers must be considered, which implies that, as compared with organophilic montmorillonite, only a limited interlamellar space in the Pd–HTs is available for the guest molecules, even if the alkyl chains are in a perpendicular orientation [66].

It is important to note that the *cis* stereoselectivities for the semihydrogenations of disubstituted acetylenes on Pd–HTs were exceptionally high, approaching 100%, which was actually experienced for the bond selectivity of styrene formation. The evidence that overhydrogenations of the reactants on both catalysts were either suppressed or nonexistent may be regarded as indirect evidence of the absence of Pd β-hydride, a potential hydrogen supply source that tends to promote oversaturation [46,67,68].

As recently suggested by Somorjai, a major challenge in future catalysis research is the achievement of 100% selectivity for the desired product, i.e., the absence of wasteful or polluting by-products. It is claimed that this goal can be attained by controlled catalyst fabrication [69,70]. In view of this perspective, our Pd–HT samples with controlled Pd particle size can be regarded as promising catalysts with improved selectivities under mild conditions, which may find further applications in the synthesis of fine chemicals.

4. Conclusions

Low-loaded, organophilic Pd–HT catalysts were synthesized in a micellar system, mediated by an anionic surfactant stabilizer. Structural investigation of the layer-structured samples revealed that regular intercalation of the Pd particles was unlikely and a considerable proportion of the Pd crystallites were situated on the external surface sites of the HT layers. For Pd–HT1, the mean Pd particle size was smaller and the size distribution was narrower than those for Pd–HT2.

The hydrophobic character and the swelling ability of the Pd–HTs made them readily applicable in liquid-phase reactions in organic solvents. Both samples proved to be efficient catalysts for the semihydrogenations of alkynes under mild conditions: for the reactants phenylacetylene and 4-octyne, marked catalytic activities were observed, and the selectivities for the formation of the main reaction products styrene and *cis*-4-octene exceeded 96%. The moderate solvent effect established for the hydrogenation of phenylacetylene on Pd–HT1 can be attributed to the effects of swelling and disaggregation, rather than to that of H_2 solubility in the dispersion medium.

In addition to the surface Pd content, interlamellar Pd particles may also participate as active sites in the above reactions. Except for the application of hexane as a solvent, the interlayer spacings of the solvated Pd–HTs were found to be large enough to accommodate each substrate. Accordingly, the pronounced decrease in the turnover rates observed for the transformation of 1-phenyl-1-pentyne, the bulkiest substrate, may be attributed to steric restrictions of reactant chemisorption, rather than to a molecular sieving effect of the catalysts. For this reaction, *cis*-alkene stereoselectivities of at least 86% were obtained. For the transformations of internal alkynes, the Pd–HT samples proved to be more stereoselective than the conventional supported Pd catalysts.

Increase of the Pd dispersion of Pd–HT resulted in an enhanced catalytic activity for all reactants, due to a site modification effect, but it had no appreciable influence on the alkene selectivity.

The exceptionally high bond selectivities and *cis*-alkene stereoselectivities of the Pd–HT catalysts may be attributed to their low metal loading and controlled Pd particle size. Further studies to extend their applications in the field of organic catalysis are currently in progress.

Acknowledgment

Financial support of the National Scientific Foundation through OTKA Grant T 042521 is gratefully acknowledged.

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