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Preparation of Organophilic Pd–Montmorillonite, An Efficient Catalyst in Alkyne Semihydrogenation

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Palladium particles incorporated into organophilic montmorillonite (Pd–M) were prepared via a novel synthetic method, mediated by a cationic surfactant stabilizer. The materials were characterized by UV–Vis, ICP-AES, and TEM. Two representative samples (Pd–M1 and Pd–M2), with metal contents of 0.1% and 0.46%, respectively, were investigated in detail. TEM measurements indicated that the diameters of the Pd particles observed were in the range 1.5–6 nm. It is suggested that most of the Pd particles are situated on the external surface of the clay lamellae. Both Pd–M samples exhibited marked catalytic activities and stereoselectivities in the liquid-phase hydrogenation of 1-phenyl-1-butyne. For the production of the *cis*-alkene stereoisomer, Pd–M2 proved to be less active but more stereoselective than Pd–M1. The stereoselectivities obtained for Pd–M2 in *n*-hexane (86–88%) were nearly as high as those experienced for the Lindlar catalyst. © 2000 Academic Press

Key Words: **montmorillonite; palladium; nanoparticles; surfactant; 1-phenyl-1-butyne; hydrogenation; stereoselectivity.**

INTRODUCTION

The preparation and catalytic application of clay–intercalated metal complexes and nanoparticles, initiated by Pinnavaia *et al.* (1, 2), have attracted considerable attention (3–9). One of the most widely used support materials, montmorillonite, belongs in the group of smectite clay minerals. Montmorillonite, a 2 : 1-type layered aluminosilicate and a good cation exchanger, permits the incorporation of various metal cations or positively charged complexes into the interlamellar space (1, 10). Metal insertion may be enhanced by utilizing the swelling property of montmorillonite (1, 11); i.e., the application of an appropriate dispersion medium gives rise to expansion of the clay lamellae and hence results in an increased basal spacing available for guest species (12, 13).

Palladium incorporation into montmorillonite has been the subject of several studies. An important preparation method is the formation of heterogenized homogeneous Pd complexes in the interlayer space of montmorillonite, subsequently applied as catalysts in the hydrogenations of unsaturated substrates (14, 15). More recently, the formation and stabilization of highly dispersed Pd particles have been investigated. Ultrafine Pd nanoparticles may be prepared with alcohols (12, 16, 17), with hydro-organoborates (18, 19), and also by sonochemical methods (20, 21). An efficient means of protecting the metal nanoparticles from aggregation is the application of cationic surfactants for stabilization (22–24). The catalytic activity of montmorillonite–intercalated Pd crystallites has been confirmed in alkene and alkyne hydrogenations (25).

Previous investigations revealed that, of all the metals studied for alkyne semihydrogenation, Pd is the most selective catalyst (26, 27). The aim of the present work was the preparation of finely dispersed Pd nanoparticles intercalated in montmorillonite by applying a cationic surfactant that renders the clay surface hydrophobic and prevents metal aggregation. The catalytic activity of the Pd–montmorillonite (Pd–M) formed was tested in the liquid-phase hydrogenation of 1-phenyl-1-butyne.

EXPERIMENTAL

Materials

The calculated amount of a 0.5–3% solution of $Pd(acac)_2$ (Aldrich) in $CHCl_3$ was added to an aqueous solution of a cationic surfactant, tetradecyltrimethylammonium bromide ($C_{14}TAB$, a Sigma product) under stirring. The concentration of the $C_{14}TAB$ solution was 10–30 times the critical micelle concentration (cmc = 3.9 mM at 298 K in H_2O). Upon reduction with an excess of 55% hydrazine dissolved in water of the bright-yellow colloidal solution obtained, a dark-brown Pd sol was formed. Pd–montmorillonite was prepared by the addition of 50–200 ml of the Pd sol to 100–500 ml of a 0.1–2% Na–montmorillonite suspension in 0.01% NaCl under vigorous stirring, which proceeded for 24 h. The reaction mixture was subsequently centrifuged with a Sorwall RC centrifuge for 30 min (3500 rpm). Any residual surfactant was removed by washing the

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product with ethanol and then with toluene, in several centrifugation–redispersion cycles. The products were air-dried and stored in a vacuum desiccator until use (28).

For comparative experiments, the Lindlar catalyst (5% $Pd/CaCO_3$ poisoned with lead, an Aldrich product) was applied.

1-Phenyl-1-butyne, the substrate for catalytic hydrogenation, was an Aldrich product of 99% purity and was used as received.

Methods

The metal contents of the Pd–M samples were obtained indirectly by monitoring the turbidity of the Pd sol before and after adsorption on montmorillonite. The measurements were carried out with a UVIKON 930 spectrophotometer operated at a fixed wavelength of 600 nm. A calibration curve indicated a linear relationship between the turbidity and the Pd concentration (29). The amount of Pd particles adsorbed on the montmorillonite was calculated from the turbidity change in the supernatant, due to adsorption.

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was employed to determine the metal contents of the Pd–M samples. The measurements were carried out with a Jobin Yvon 24 sequential ICP-AES spectrometer at 229.7 nm. Before investigation, the samples were dissolved in a 1 : 2 mixture of aqua regia and 0.5 M $(NH_4)HF_2$. The Pd contents were obtained from the emission intensities by means of a calibration curve.

TEM investigations were performed with a Philips C-10 transmission electron microscope at 100 kV of accelerating voltage, with a magnification of 10^5. The samples were dispersed in ethanol and subsequently mounted and air-dried on a plastic film supported by a Formvar grid. The mean particle diameters d were determined as number-average values $(\sum n_i d_i / \sum n_i)$ from the magnified TEM images, for 200 particles on average. As a consequence of the spherical symmetry of the Pd particles observed, the active surface area of the Pd (D_S) was calculated as $D_S = 0.885/d$ (30).

The test reaction was the hydrogenation of 1-phenyl-1-butyne, performed in an automated liquid-phase reactor at 10^5 Pa. For each measurement, the mass of catalyst used was 10 mg and the amount of reactant related to the Pd content of the catalyst was S : C = 2500 (mol of substrate/mol of Pd). Before reaction, the sample was pretreated in 10^5 Pa of H_2 at 298 K for 1 h, 1 cm^3 of solvent was then added, and further treatment in H_2 was applied under stirring (1400 rpm) at the same temperature for 45 min. Stirring was maintained after introduction of the reactant and the reaction was monitored with a PC. After the reaction had been completed, the catalyst was removed by gravity filtration and the filtrate was analyzed to establish the product distribution.

The reaction products were identified with an HP 5890 GC and an HP 5970 MSD apparatus, a DB-1 capillary column (i.d. = 0.25 mm, $l = 60$ m) being used for separation. Quantitative analysis was performed with an SRI 8610 A gas chromatograph equipped with a DB-Wax capillary column (i.d. = 0.53 mm, $l = 30$ m) and FID. The experimental error in the product analysis was ±0.01–0.15%.

RESULTS AND DISCUSSION

The proposed mechanism for the successive formation of the Pd hydrosol and the Pd–organoclay is illustrated in Fig. 1. While the precursor $Pd(acac)_2$ is readily soluble in $CHCl_3$, it is almost insoluble in water. To accomplish the dissolution of $Pd(acac)_2$ in an aqueous system, $C_{14}TAB$ is added, which tends to increase the apparent solubility of $CHCl_3$ in water. If the concentration of the surfactant exceeds the cmc (the concentration at which association of the surfactant molecules, i.e., micelle formation, occurs), an aqueous colloidal solution of $Pd(acac)_2$ previously dissolved in $CHCl_3$ may be formed via the solubilization effect. The latter means the formation of a thermodynamically stable colloidal solution in the presence of surfactant molecules.

In our case, according to Fig. 1, the apolar system $Pd(acac)_2$ dissolved in $CHCl_3$ is situated in the internal apolar part of the micelles formed in the aqueous solution. The UV–Vis spectrum of $Pd(acac)_2$ indicated a shift in the absorbance maximum of the micellar solution (340 nm) as compared with that in pure $CHCl_3$ (327 nm). This may be attributed to a change in the microenvironment of $Pd(acac)_2$, induced by solubilization or, more likely, by the formation of an adduct between the surfactant and the palladium salt (21, 31). The addition of an aqueous hydrazine solution to the micellar system resulted in the

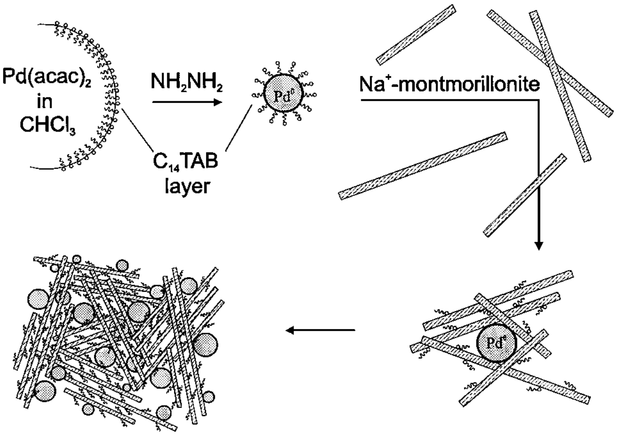

FIG. 1. Schematic illustration of the mechanism suggested for the successive formation of Pd–hydrosol and Pd–montmorillonite in a micellar system.

TABLE 1

Characterization of Organophilic Pd–Montmorillonite Catalysts

Sample	Pd [%] UV–Vis	Pd [%] ICP-AES	*d* [nm] TEM	D_S
Pd–M1	0.09	0.11	2.42	0.36
Pd–M2	0.51	0.42	3.68	0.24

formation of Pd^0 nanoparticles, stabilized both sterically and electrostatically by the cationic surfactant molecules adsorbed on the surface of the particles (Fig. 1). The stabilizing effect of the C_{14}TAB molecules prevented the aggregation of nanosized Pd clusters.

Pd–M was obtained by mixing the Pd hydrosol with a dilute Na^+–montmorillonite suspension. The reaction of Na^+–montmorillonite with the stabilizing surfactant molecules resulted in the formation of organophilic alkylammonium montmorillonite, with the simultaneous release and the subsequent deposition of the Pd nanoparticles on the surface of the clay lamellae (Fig. 1). It should be stressed that the surfactant molecules had a key role in the preparation of Pd–M since they ensured both the stabilization of the Pd particles and the cationic exhange of the clay host by rendering it hydrophobic and thus readily applicable in organic media.

Two Pd–M samples with different levels of metal loading were selected for further investigations. Table 1 lists the mean particle diameters of the samples, obtained from TEM, and the Pd contents, determined by UV–Vis spectroscopy and ICP-AES. The Pd contents obtained by the two methods are in good agreement, and the actual Pd loadings of Pd–M1 and Pd–M2 are therefore taken as 0.1% and 0.46%, respectively.

TEM measurements revealed the presence of spherical, monodispersed Pd particles in the range 1.5–6 nm, situated mostly on the external surface sites of the montmorillonite. The particle size distributions are displayed in Figs. 2 and 3.

Figures 2 and 3 indicate a fairly narrow range of particle diameters for both Pd–M samples. For Pd–M1, the majority of the Pd nanoparticles fell in the range 1–3 nm, and the largest particle diameter observed was 5 nm. For Pd–M2, a different size distribution was obtained, which suggested the appearance of a small amount of Pd particles larger than 6 nm. This may account for an increased mean particle diameter as compared with Pd–M1, which resulted in a lower active surface area of Pd, as can be seen in Table 1. The occurrence of a large amount of ultrafine (1–2 nm) Pd particles for Pd–M2 may be attributed to the stabilizing effect of the surfactant, which prevents aggregation if the metal loading is increased. In fact, only a few aggregates appeared, whereas the frequency of the 1- to 2-nm particles increased considerably.

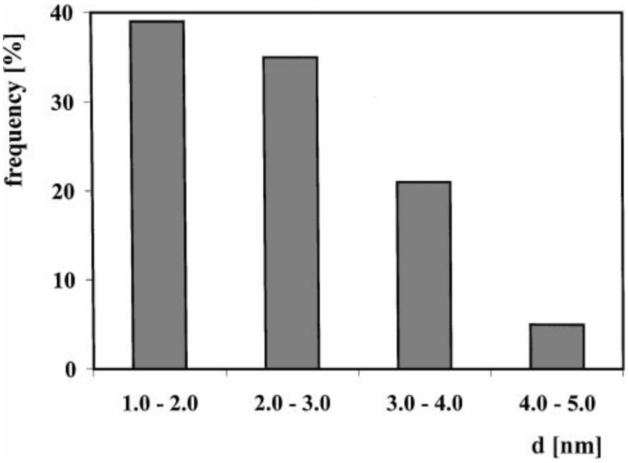

FIG. 2. Particle size distribution obtained for Pd–M1.

Montmorillonite is well known to be a hydrophilic clay mineral that is usually employed in aqueous systems (1, 10). However, organophilic Pd–M samples may be readily dispersed in a variety of organic solvents generally used in liquid-phase catalytic hydrogenation reactions. The transformation of 1-phenyl-1-butyne on Pd–M1 at 298 K is illustrated in Fig. 4. The reaction was carried out in tetrahydrofuran (THF), which led to a considerable swelling of the clay host (the basal spacings d_L obtained from previous XRD data for Pd–M1 in THF and in the dry state were 3.74 and 1.72 nm, respectively) (13).

Pd–M1 exhibited an appreciable catalytic activity in the hydrogenation of 1-phenyl-1-butyne. The conversion increased rapidly with the reaction time, and at 90 min, transformation was complete. After this time, there was no appreciable change in the product distribution. With regard to the product selectivities, the main reaction pathway was the semihydrogenation of 1-phenyl-1-butyne, resulting in the formation of *cis*- and *trans*-alkenes, with a

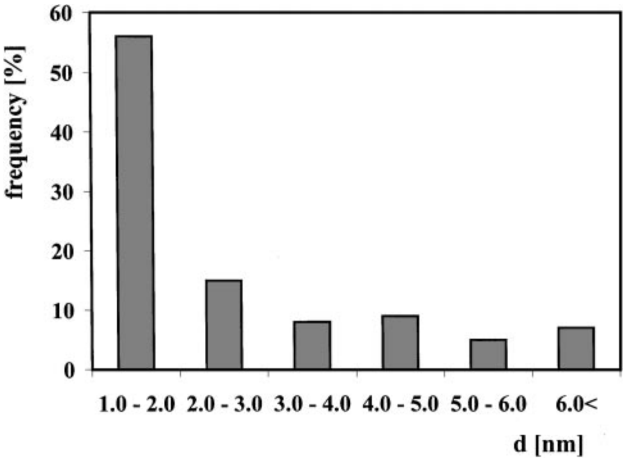

FIG. 3. Particle size distribution obtained for Pd–M2.

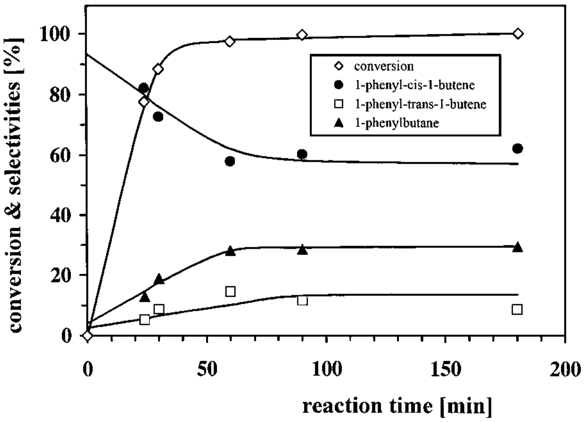

FIG. 4. Transformation of 1-phenyl-1-butyne on Pd–M1 as a function of the reaction time. Mass of catalyst, 10 mg; $T = 298$ K; $p = 10^5$ Pa; solvent, 1 cm^3 of THF; S : C = 2500.

predominance of the *cis* isomer. The highest *cis* stereoselectivities were observed at the beginning of the reaction. The selectivity of the formation of the overhydrogenation product 1-phenylbutane increased at the expense of 1-phenyl-*cis*-1-butene and reached its highest value at 60 min. The selectivities of the formation of both 1-phenylbutane and the *trans* stereoisomer exhibited no appreciable change after 90 min, with the amount of 1-phenyl-*trans*-1-butene being substantially lower in the reaction. It is apparent that a prolonged reaction time is not favoured in terms of *cis* selectivity since it tends to reinforce the overhydrogenation of 1-phenyl-*cis*-1-butene.

Previous literature results indicated that the application of subambient temperature and an apolar solvent tends to increase the stereoselectivity of *cis*-alkene formation (32). We therefore changed the dispersion medium to *n*-hexane and studied the temperature dependence by applying a reaction time of 60 min. The results obtained are illustrated in Fig. 5.

It is clear that the introduction of *n*-hexane decreased the conversion of 1-phenyl-1-butyne to some extent. This may be explained by the evidence that in *n*-hexane no swelling of Pd–M1 occurred ($d_L = 1.92$ nm), which implies that the clay lamellae are more aggregated as compared with those in THF. It follows that the exposed Pd surface area available for reactant molecules is lower in *n*-hexane than in THF. However, the application of *n*-hexane had a positive effect on the stereoselectivity of 1-phenyl-*cis*-1-butene formation, which displayed little variation with the reaction temperature. Nevertheless, the highest value of 82% was observed at the subambient temperature of 283 K. Similarly, the low stereoselectivity of *trans*-alkene formation (3–6%) underwent no significant change upon an increase of the temperature. There was no significant change of conversion below 298 K, but a marked increase was experienced at this temperature. It appears that reduction of the reaction temperature neither eliminates nor appreciably decreases the formation of 1-phenylbutane, which suggests that the formation of stereoisomeric alkenes and 1-phenylbutane is more likely to occur via simultaneous processes than in consecutive reactions (27, 33). Although an augmentation of alkane selectivity in response to a temperature increase could have been expected (27, 34), there was no evidence of this in our case.

Figure 6 demonstrates that the catalytic activity of Pd–M2 in THF was lower than that of Pd–M1. This may be ascribed to the increase in the mean particle size of the Pd particles (Figs. 2 and 3), which implies a lower active metal surface area available for reactants, despite the appearance of ultrafine Pd particles (Table 1). Nevertheless, a full transformation of the reactant can be achieved over a period of 180 min. With regard to the product selectivities, the stereoselective formation of 1-phenyl-*cis*-1-butene is clearly established; it was more pronounced than that for Pd–M1. The variations of the product selectivities with

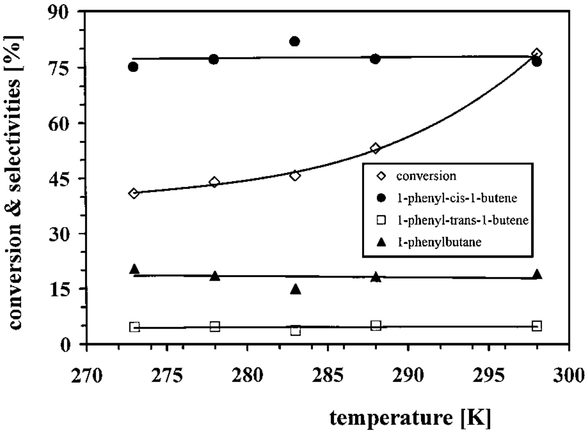

FIG. 5. Transformation of 1-phenyl-1-butyne on Pd–M1 as a function of the reaction temperature. Mass of catalyst, 10 mg; $p = 10^5$ Pa; reaction time, 60 min; solvent, 1 cm^3 of *n*-hexane; S : C = 2500.

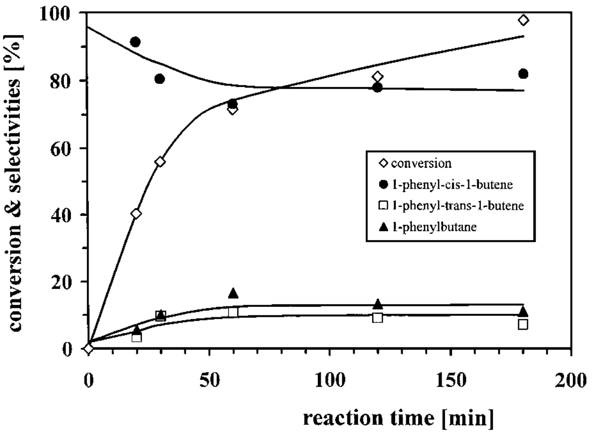

FIG. 6. Transformation of 1-phenyl-1-butyne on Pd–M2 as a function of the reaction time. Mass of catalyst, 10 mg; $T = 298$ K; $p = 10^5$ Pa; solvent, 1 cm^3 of THF; S : C = 2500.

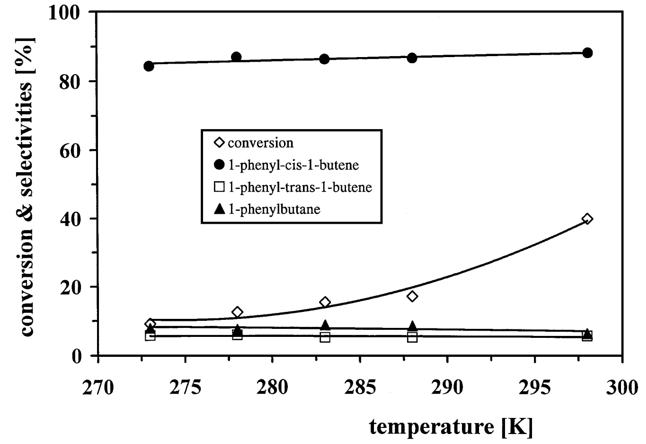

FIG. 7. Transformation of 1-phenyl-1-butyne on Pd–M2 as a function of the reaction temperature. Mass of catalyst, 10 mg; $p = 10^5$ Pa; reaction time, 60 min; solvent, 1 cm^3 of *n*-hexane; S : C = 2500.

reaction time were found to be similar to those obtained for Pd–M1. However, the selectivity of 1-phenylbutane formation was significantly lower for Pd–M2 than for Pd–M1 and was very close to that of the *trans* isomer. It follows that overhydrogenation is less of a problem for Pd–M2, which was found to be more stereoselective than Pd–M1. As revealed by Fig. 7, the stereoselectivity of *cis*-alkene formation may be further increased by applying *n*-hexane as a dispersion medium.

The most important observation provided by Fig. 7 is the remarkably high stereoselectivity of 1-phenyl-*cis*-1-butene formation, which remains practically unchanged (86–88%) throughout the entire temperature range. For Pd–M2, the conversion of 1-phenyl-1-butyne at 298 K for 60 min decreased from 71% to 41% when the dispersion medium was changed from THF to *n*-hexane (see also Fig. 6). This loss of activity was far more pronounced than that observed for Pd–M1 under the same conditions (97% ⇒ 79%). Moreover, the application of subambient temperatures decreased the catalytic activity of Pd–M2 even further. On the other hand, no noteworthy changes in the selectivities of the minor products as a function of temperature could be detected. Whereas the stereoselectivities obtained for 1-phenyl-*trans*-1-butene were very similar for the two Pd–M samples, the selectivity of the overhydrogenation product for Pd–M2 was decreased considerably (6–9%). It follows that Pd–M2 may be regarded as an extremely efficient catalyst in the stereoselective semihydrogenation of 1-phenyl-1-butyne. The initial rates and the product selectivities obtained at the same conversion level for Pd–M1 and Pd–M2 in THF and *n*-hexane are listed in Table 2.

For both THF and *n*-hexane, the initial rates obtained for Pd–M1 were higher than those observed for Pd–M2, which confirms that the increase in the mean particle diameter of Pd decreases the catalytic activity. Moreover, a pronounced solvent effect is suggested by the differences in the initial rates determined in THF and *n*-hexane. As indicated by the basal spacings mentioned above, swelling of the clay host was much more important in THF than in *n*-hexane. The increased swelling observed in THF is accompanied by a considerable disaggregation of the clay lamella packages. Hence, the amount of active Pd particles exposed to the reactant molecules is also increased, despite the evidence that the Pd particles formed were mainly situated on the external sites of the montmorillonite. For a given catalyst, the stereoselectivities of *cis* alkene formation in different solvents were very close (in fact, they were exactly the same for Pd–M2), and thus they were clearly unaffected by the dispersion medium. The stereoselectivities obtained for the formation of 1-phenyl-*cis*-1-butene were in the same order as those reported for the semihydrogenation of phenylacetylene on hydrophilic Pd–montmorillonite (25). However, the initial rates determined for the present Pd–Ms were considerably higher, especially for Pd–M1. Thus, it is concluded that hydrophobic Pd–M samples are more efficient catalysts than hydrophilic ones in alkyne semihydrogenation.

As reported in the literature, *trans*-alkenes are always formed in the hydrogenation of alkynes, either as initial products or as a result of isomerization of the *cis* stereoisomer (27, 35). It is generally accepted that direct *trans*-alkene formation may occur via the addition of molecular hydrogen to the adsorbed alkyne molecule (36). In our case, the experimental evidence indicated that a small amount of *trans*-alkene was always formed in the reaction mixture before the alkyne had been consumed. On the other hand, a drop in the *cis* stereoselectivity parallel to an increase in the *trans* stereoselectivity was observed for both Pd–M samples at reaction times between 30 and 60 min (Figs. 4 and 6), which suggested that *cis* → *trans* isomerization took place. Hence, the current study supported the evidence that 1-phenyl-*trans*-1-butyne may be formed via both routes (35). Nevertheless, it should be stressed that, for Pd–M2, the isomerization pathway was far less important. This may be related to the large number of ultrafine Pd particles (see Fig. 3). The activation energies obtained from the Arrhenius plots were 91.5 and 88.5 kJ mol^{-1} for Pd–M1 and Pd–M2, respectively. Such high values may reflect the adsorption

TABLE 2

Initial Rates and Selectivities of Pd–M1 and Pd–M2 Determined at 298 K in THF and *n*-Hexane

Sample	Solvent	Conv. [%]	r_i [cm^3/(min mmol of Pd)]	$S_{\text{total alkene}}$ [%]	$S_{\text{cis}}/S_{\text{(cis+trans)}}$
Pd–M1	THF	78	1789	84	0.929
Pd–M1	*n*-Hexane	78	842	81	0.938
Pd–M2	THF	40	1224	94	0.936
Pd–M2	*n*-Hexane	40	369	94	0.936

TABLE 3

Transformation of 1-Phenyl-1-butyne on Lindlar Pd and Pd–M2

	Conversion and selectivities [%] Lindlar Pd[a]				Conversion and selectivities [%] Pd–M2[b]			
T [K]	Conv.	S_{cis}	S_{trans}	$S_{cis}/S_{(cis+trans)}$	Conv.	S_{cis}	S_{trans}	$S_{cis}/S_{(cis+trans)}$
278	10	93	3	0.969	13	87	6	0.925
283	17	93	3	0.969	15	86	5	0.945
298	42	92	5	0.948	41	88	6	0.936

[a] $m = 10$ mg; solvent, 1 cm^3 of n-hexane; S : C = 250; reaction time, 60 min.
[b] $m = 10$ mg; solvent, 1 cm^3 of n-hexane; S : C = 2500; reaction time, 60 min.

heat of the substrate at saturation coverage, as reported for the liquid-phase hydrogenation of 2-hexyne, where an equally high activation energy of 87.9 kJ mol^{-1} was determined (37).

For Pd catalysts, the Pd–H system readily undergoes conversion into the β-hydride, which may affect the catalytic performance (38). In our case, the Pd contents of both Pd–M samples appear as small clusters, and according to the mean particle diameters displayed in Table 1, they are very unlikely to form β-hydrides, as reported by Nandi *et al.* (39). Hence, our experimental results are in accordance with those of previous studies on the semihydrogenation of phenylacetylene, where it was suggested that the best stereoselectivities were obtained for highly dispersed Pd particles, which displayed no β-hydride formation at 298 K (40).

The experimental data in Table 3 indicate that the stereoselectivity of Pd–M2 is comparable with that of the Lindlar catalyst, which is considered to be the most stereoselective of all Pd catalysts investigated in alkyne semihydrogenation (27).

There was no appreciable difference between the conversions obtained for the two samples, and the stereoselectivities of 1-phenyl-*cis*-1-butene formation on Pd–M2 approached those observed for Lindlar Pd reasonably well, especially at 298 K. The efficiency of Pd–M2 is further supported by the evidence that the reaction on the Lindlar catalyst was performed with S : C = 250, which was 1 magnitude lower than that for Pd–M2. That is, to achieve a similar transformation for a given amount of substrate, Pd–M2 may be applied in a considerably smaller amount than the Lindlar catalyst.

CONCLUSIONS

Pd–montmorillonite was prepared via a novel synthetic method that provided finely distributed Pd particles situated mostly on the external surface of the clay lamellae. The surfactant $C_{14}TAB$ had a key role in preparation since it ensured both the stabilization of nanosized Pd clusters and the formation of organophilic montmorillonite by cationic exchange. The catalytic activities of both Pd–M samples studied were confirmed in the liquid-phase semihydrogenation of 1-phenyl-1-butyne. Nevertheless, their catalytic performances were different. Pd–M2, which was less active but more stereoselective than Pd–M1, is regarded as more efficient for the above reaction. At the same conversion level, the application of n-hexane as a dispersion medium afforded stereoselectivities similar to those obtained in THF, and the role of subambient temperatures was rather insignificant. As a consequence of the high dispersion of the Pd particles, the formation of β-hydride is unlikely. The amount of Pd–M2 required for similar catalytic performance was considerably lower than that of the Lindlar catalyst.

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