Preparation of Ultrafine Palladium Particles on Cationic and Anionic Clays, Mediated by Oppositely Charged Surfactants: Catalytic Probes in Hydrogenations

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Finely divided Pd particles (2−3 nm in diameter) were synthesized by the reduction of Pd^{2+} precursor ions in the presence of cationic (myristyltrimethylammonium bromide, MTA^+Br^-) or anionic (sodium dodecyl sulfate, Na^+DS^-) surfactants. The protective adsorption layer of the ionic surfactants around the particles ensured the long-term stability of the aqueous dispersions. When the palladium hydrosol stabilized with MTA^+Br^- was mixed with an aqueous suspension of sodium montmorillonite, Na^+MM^- (a cationic clay), the cation-exchange reaction between Na^+ and MTA^+ rendered the montmorillonite surface hydrophobic, in parallel with the incorporation of the released Pd particles into the MTA^+MM^- organoclay host. In a similar way, after addition of the palladium hydrosol stabilized with Na^+DS^- to an aqueous suspension of hydrotalcite nitrate, $HT^+NO_3^-$ (an anionic clay), the ion exchange between NO_3^- and DS^- resulted in the formation of a hydrophobic clay, HT^+DS^-, with simultaneous deposition of the released Pd particles onto the clay lamellae. The low-loaded, highly dispersed Pd-organoclay materials displayed extremely high catalytic activities under mild conditions in the liquid-phase hydrogenations of styrene, hex-1-ene, and cyclohexene. Furthermore, the catalysts exhibited high selectivities for the partial hydrogenation of 1-phenyl-1-pentyne to 1-phenyl-*cis*-1-pentene. These high activities and selectivities were explained in terms of the high degree of dispersion of the Pd particles and the hydrophobic nature of the catalysts.

Introduction

Montmorillonite (MM), a crystalline aluminosilicate, is a clay mineral of natural origin.[1−6] Hydrotalcite-type (HT) materials (also known as layer double-metal hydroxides) are synthetic, crystalline, mixed magnesium/aluminum hydroxides.[5−10] MM and HT have similar, expandable two-dimensional (2D) layer structures. In consequence of isomorphous substitution, the net charge on the basal planes is negative for MM but positive for HT. For both materials, the permanent surface charge is compensated by oppositely charged, exchangeable interlayer ions. Hence, MM and HT may be regarded as representative examples of cationic clays and anionic clays, respectively. Although MM and HT possess different compositional variables, crystal lattice parameters, and surface specificities, these materials also exhibit many similar features: the small size of the platelike particles (a few micrometers in diameter); the subcolloidal single-layer thickness (ca. 1 nm); the ability to swell, depending on the solvent properties; the permanent and variable surface charges; the ion-exchange propensity (with an effective exchange capacity in the order of 1 mequiv g^{-1}); a relatively small Brunauer−Emmett−Teller (BET) surface area (in the order of 10 $m^2\,g^{-1}$); a high crystal geometric surface area (hundreds of meters squared per gram), which may become fully accessible for probe molecules after swelling; molecular sieving properties; etc.

Among the wide range of industrial applications, clays have attracted interest in heterogeneous catalysis because of their actual and potential uses as catalysts and catalyst supports.[2−10] To date, a variety of methods have been developed to introduce catalytically active noble metal species into cationic clays. Rh,[11,12] Pd,[13,14] and Ru organocomplexes[15] have been chemically anchored to internal surface sites of cationic clays to produce heterogenized homogeneous catalysts. The ion exchange of Na^+ ions in smectite clays (MM or hectorite) for cationic Pt,[16] Ru,[17] and Pd complexes[18,19] or Cu^{2+} [20,21] and the subsequent

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reduction of these interlayer cations afforded highly dispersed metal clusters, mostly situated on the internal surface sites of the clay. In previous studies, we reported on the in situ generation of Pd nanoparticles on alkyl-ammonium$^+$MM$^-$,[22,23] a method based on the selective sorption of a reducing agent from dilute solution at the solid/solution interface, thereby providing a suitable environment for the reduction of a Pd^{2+} precursor within the adsorption layer of the organoclay host. More recently, we reported on a surfactant-mediated synthesis of orga-nophilic Pd−MM, where a cationic surfactant facilitated both the formation of ultrafine Pd particles and the subsequent deposition of the preformed particles on the surfaces of the clay lamellae.[24,25]

Anionic clays with noble metal ions in the HT crystal lattice have been prepared via the coprecipitation of Mg and Al salts with some precursor compounds containing Rh^{3+}, Ir^{3+}, Ru^{3+}, Pd^{2+}, or Pt^{2+}.[26,27] The intercalation of complex anions and metalloorganic complexes by an anion-exchange reaction in the HT host has also been reported.[7−9,28,29]

The present work describes a novel synthetic route for the generation of finely divided Pd particles in anionic and cationic clay matrixes and demonstrates the versatil-ity of the resulting hydrophobic Pd-clay materials in terms of their activity and selectivity in the catalytic hydroge-nations of alkenes and alkynes in the liquid phase.

Experimental Section

Cationic Clay. Sodium montmorillonite (Na$^+$MM$^-$) was provided by Süd-Chemie AG, Germany. Fine particles ($d < 2$ μm) were obtained by fractionation. The cation-exchange capacity (CEC) was determined after organophilization by using a MOM Q-1500 D derivatograph and an Euroglas TOC 1200 total organic content analyzer. First, the Na$^+$ was exchanged for myristylt-rimethylammonium surfactant cations (MTA$^+$). The clay orga-nocomplex was then purified by Soxhlet extraction with a 1:1 mixture of 2-propanol:water and finally dried at 353 K under vacuum. Thermogravimetry and TOC analysis yielded CEC = 1.13 mequiv g^{-1} to within 3%. The BET surface area, determined with a Micromeritics Gemini 2375 gas sorption apparatus, was 27 m^2 g^{-1} with respect to N$_2$ at 77 K.

Anionic Clay. The chemicals used for the preparation of the mixed magnesium/aluminum hydroxide were of p.a. purity and purchased from Reanal, Hungary. The HT material with exchangeable NO$_3^-$ counterions was synthesized by a standard method.[28] Aqueous solutions of Al(NO$_3$)$_3$·6H$_2$O and Mg(NO$_3$)$_2$·9H$_2$O, in a Mg:Al molar ratio of 2:1, were added dropwise to an aqueous solution of NaOH during vigorous stirring. The reaction was left to proceed for 5 h under N$_2$ at 333 K. The pH was continuously monitored and maintained between 9 and 10 by using aqueous NH$_4$OH and HNO$_3$ solutions, as required. After

the reaction was completed, the white precipitate was washed with distilled water in several centrifugation/redispersion cycles and stored in an aqueous suspension until use. The powder X-ray diffraction (XRD) pattern, determined by using a Philips PW diffractometer (40 kV, 35 mA, Cu Kα radiation), confirmed the formation of a well-crystalline HT phase in the nitrate form (the basal spacing of the dry HT$^+$NO$_3^-$ was 0.78 nm, as compared to 1.24 nm for Na$^+$MM$^-$). The anion-exchange capacity (AEC) was determined in a manner similar to the CEC of the cationic clay, but dodecyl sulfate (DS$^-$) was used for anion exchange. TOC analysis yielded an effective AEC of 1.77 mequiv g^{-1}. The BET surface area was found to be 12 m^2 g^{-1}.

Palladium Hydrosols. Surfactant-stabilized ultrafine Pd particles were prepared in an aqueous media via the reduction of palladium(II)−acetylacetonate (Pd(acac)$_2$, 99%, Aldrich) by hydrazine (5 M in water, Fluka) in the presence of myristylt-rimethylammonium bromide (MTA$^+$Br$^-$, 99%, Sigma) or sodium dodecyl sulfate (Na$^+$DS$^-$, 99%, Sigma). Water is a poor solvent for Pd(acac)$_2$; the latter was therefore first dissolved in chloroform (1 w/v %) and then introduced into the aqueous surfactant solution to produce a normal micellar solution.[24,25] Typically, the micellar system was composed of Pd(acac)$_2$ (from 0.1 to 1 mM); a 10-fold excess of hydrazine; and MTA$^+$Br$^-$ (in the order of >40 mM) or Na$^+$DS$^-$ (8 mM). Reduction was complete after a few minutes, as confirmed by UV−vis spectrophotometry (UVIKON 930). The particle sizes were determined by using a Philips C-10 transmis-sion electron microscope (TEM) operated at 100 kV. Particles were deposited on a Formvar-covered copper grid. For each sample, over 200 particles were counted, and data processing was effected by the UTHSCSA Image Tool program.

Pd-Organoclay Materials. The palladium hydrosol (100−800 mL, 10^{-3}−10^{-2} wt % Pd), stabilized by MTA$^+$Br$^-$ (>40 mM) was added in a few minutes to an aqueous suspension of Na$^+$MM$^-$ (100−1000 mL, ca. 0.5 wt % MM). The palladium−surfactant−clay system was left under vigorous stirring overnight. Similarly, the palladium hydrosol, stabilized with Na$^+$DS$^-$, was mixed with an aqueous suspension of HT$^+$NO$_3^-$ over 10 h. The ion exchange of Na$^+$ with the stabilizing MTA$^+$ and the ion exchange of NO$_3^-$ with the stabilizing DS$^-$ resulted in the formation of hydrophobic clay organocomplexes with simultaneous, irreversible deposition (adsorption) of the Pd particles onto the clay surfaces. The initial brownish color of the supernatant liquid became progressively less intense as the formation of the Pd-clay material proceeded. The supernatant was even completely transparent at a suf-ficiently low palladium to clay ratio. The Pd-organoclay samples (gray to black in color) were purified in ethanol by centrifugation/redispersion cycles and finally dried at 353 K under vacuum. The basal spacings were measured by XRD; the Pd contents were determined by inductively coupled plasma atomic emission spectroscopy at 229.7 and 324.3 nm (ICP-AES, Jobin Yvon 24). The morphology and the size distribution of the Pd particles were reanalyzed in terms of new TEM images.

Two Pd−MM (designated Pd−MM1 and Pd−MM2) and two Pd−HT samples (Pd−HT1 and Pd−HT2) were selected for catalytic test reactions. The mean diameters of the Pd particles and the metal contents of the catalysts are listed in Table 1.

Catalytic Test Reactions. The catalytic activities of the Pd-organoclay materials were investigated in the liquid-phase hydrogenations of styrene, hex-1-ene, and cyclohexene (99+%, Aldrich). The reactions were carried out at 298 K and 101 kPa of H$_2$ in an automated vibration reactor. The experimental assembly is sketched in Figure 1. The catalyst sample was evacuated in a glass reaction vessel and pretreated with static hydrogen for 1 h, followed by hydrogen treatment in the slurry under vigorous stirring for another 1 h prior to the injection of the substrate. Typically, the reaction vessel contained 1 mL of solvent (toluene), 0.1 mL of substrate, and a calculated amount of catalyst to give a substrate to catalyst molar ratio (S:C) of 2000. An eccentric motor was used in the hydrogenator, which provided fast and effective stirring (shaking) to eliminate diffusion control. The reaction vessel was designed to minimize creeping of the catalyst. The route of the hydrogen supply from the hydrogen chamber (high-pressure side) toward the reaction vessel (atmospheric-pressure side) was controlled by a pressure regula-tor that separated the atmospheric-pressure side from the high-pressure side in the system. In this arrangement, a constant

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Table 1. Characterization of Pd-Organoclay Catalysts

catalyst code no.	Pd content (%)[a]	Pd particle diameter (nm)[b]	TOF (s⁻¹)			$C_H = 50\%$[d]	
			styrene[c]	hex-1-ene[c]	cyclohexene[c]	S_B (%)[e]	S_S (%)[f]
Pd−MM1	0.11	2.4 ($\sigma = 0.59$)	73.8	27.3	2.7	89.0	96.7
Pd−MM2	0.40	2.5 ($\sigma = 0.58$)	35.9	24.9	3.2		
Pd−HT1	0.10	2.3 ($\sigma = 0.58$)	19.2	7.0	0.4	92.1	96.9
Pd−HT2	0.42	3.2 ($\sigma = 0.94$)	2.6	2.5	0.3		

[a] Obtained from ICP-AES. [b] Obtained from TEM. [c] Apparent TOF. [d] Conversion = [1-phenyl-1-pentyne (transformed)]/[1-phenyl-1-pentyne (initial)]. [e] Bond selectivity = 1-phenyl-1-pentene/(1-phenyl-1-pentene + 1-phenyl-1-pentane). [f] Stereoselectivity = 1-phenyl-*cis*-1-pentene/(1-phenyl-*cis*-1-pentene + 1-phenyl-*trans*-1-pentene).
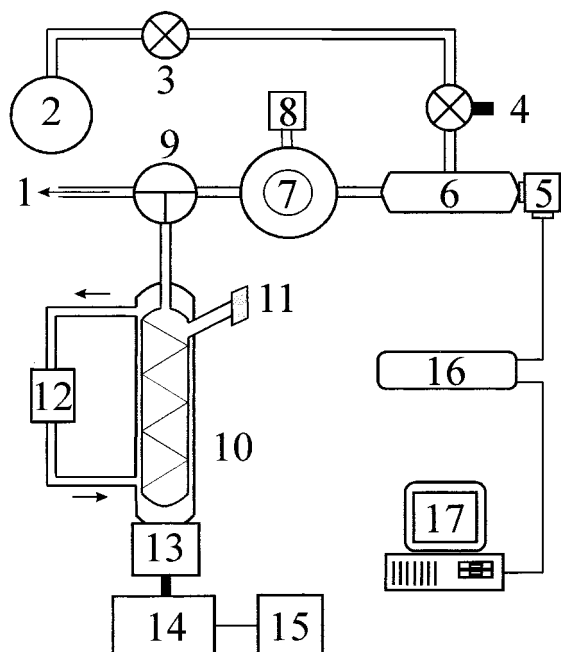
Figure 1. Experimental setup of the hydrogenator. (1) Vacuum piping, (2) hydrogen reservoir, (3) two-way valve, (4) metering valve, (5) pressure transmitter, (6) high-pressure hydrogen chamber, (7) pressure regulator, (8) pressure gauge, (9) three-way valve, (10) reaction vessel, (11) septum, (12) thermostat, (13) rubber cup, (14) eccentric motor, (15) variable-speed motor controller, (16) pressure transmitter interface, and (17) PC.

pressure was maintained during the reaction because the hydrogen consumption in the reaction vessel was balanced by the pressure regulator at the expense of the high-pressure side. The hydrogen chamber was connected to a pressure transmitter, which in turn was interfaced to a PC. The hydrogen uptake (the conversion of the substrate) in the slurry was continuously recorded at a data collection frequency of 1 s⁻¹. The reaction products were identified with a Hewlett Packard GC−MS apparatus (HP 5890 GC and HP 5970 MSD). Quantitative analysis was performed with an SRI 8610 A gas chromatograph.

The selectivities of two low-loaded catalysts, Pd−MM1 and Pd−HT1, were investigated in the hydrogenation of 1-phenyl-1-pentyne (98+%, Aldrich). The reactions were carried out in 1 mL of tetrahydrofuran (THF) at 298 K and 101 kPa of H₂. For Pd−MM1, 5 mg of catalyst was used, and the amount of substrate added was calculated to give S:C = 7500. For Pd−HT1, 10 mg of catalyst was used, and S:C = 2500. The reactions were terminated at 10, 30, 60, 90, and 120 min for sampling. For each measurement, freshly prepared slurry was used. The hydrogenation products were analyzed by GC−MS, and the conversions and selectivities were calculated.

Results and Discussion

Surfactant-Mediated Synthesis of Pd-Organoclay Materials. The synthesis method (described in the Experimental Section) produced palladium hydrosols, which exhibited high stability over a period of weeks. In general, fairly monodispersed, quasispherical Pd particles were obtained with mean diameters ranging from 1.5 to 8 nm, depending on the experimental conditions. We experienced that the (apparent) solubility of chloroform in water increased considerably when a sufficient quantity of surfactant was present in the aqueous phase. It is tempting to assume that this solubilization effect allows the preparation of an aqueous colloidal solution of Pd-(acac)₂ previously dissolved in chloroform[24] and that each particle is formed from a single micellar microdomain (inner pool). However, a systematic variation in the particle diameter with the (otherwise low) chloroform content of the micellar system was not observed, suggesting that the formation of Pd particles is not restricted to confined geometries (micellar core), but some sort of limited aggregation process ("arrested growth") takes place when the particles are formed. The role of the chloroform seems to be restricted to keeping the precursor in a molecularly dispersed state. In fact, it has been shown that compartmentalization is not a prerequisite for nanoparticle formation in media-containing surfactants[30] and that the limited aggregation of zerovalent metal atoms should be associated with the strong and rapid adsorption of the surfactants on the nascent particles with which they are in close contact from a very early stage of the reaction. The proposed mechanisms for surfactant-mediated synthesis of metallic particles are often controversial, even for similar preparation methodologies, and no definite conclusions can be drawn for the present micellar systems either. The findings of a comparative study on the conditions of Pd particle formation in the presence of anionic or cationic surfactants, with particular attention to the control over the particle size in terms of precursor concentration, the surfactant concentration, the length of the surfactant tails (including MTA⁺Br⁻ and Na⁺DS⁻ homologues), and the strength of the reducing agent, will be published shortly in a separate paper.

Ionic surfactants have been used for the stabilization of Pd (and related metallic) particles in various synthetic routes and under various experimental conditions, including organic media,[31,32] aqueous media,[33,34] heterogeneous biphasic systems,[35,36] and microemulsions.[37−40] For

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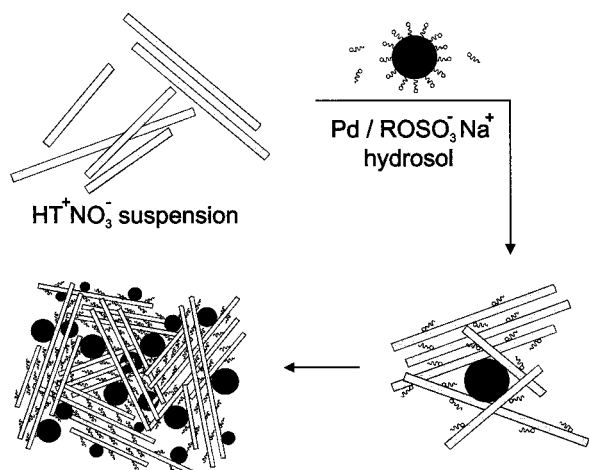
Figure 2. Proposed mechanism for the formation of an organophilic Pd−HT material after the addtion of a palladium hydrosol stabilized by an anionic surfactant to an aqueous suspension of a HT anion exchanger.

aqueous micellar systems, we propose a mechanism for the interaction of Pd clusters stabilized by anionic or cationic surfactants with oppositely charged hydrophilic clay surfaces, ultimately leading to the formation of Pd-organoclay materials. The proposed mechanism is sketched in Figure 2 for Pd−HT. After the addition of an aqueous $HT^+NO_3^-$ suspension to the palladium hydrosol stabilized by the amphiphil Na^+DS^-, the ion-exchange reaction between the DS^- surrounding the Pd particles and the NO_3^- of the HT plates renders the HT surface hydrophobic with simultaneous deposition of the released Pd particles onto the clay host. In a similar way, if a Na^+MM^- suspension is mixed with a palladium hydrosol stabilized by MTA^+Br^-, the cation-exchange reaction between the MTA^+ adsorbed on the surface of the Pd particles and the Na^+ of the hydrophilic clay results in the formation of hydrophobic MM, accompanied by the adsorption of the bare Pd particles on the silicate layers.[24,25] As the ion-exchange reaction proceeds, the decomposition of the protective surfactant layer around the Pd clusters increases the surface free energy of these clusters considerably. Restabilization is achieved as they are adsorbed on the surface of the clay lamellae. In a series of blank experiments, the native clay was treated with an aqueous surfactant solution, in the absence of Pd particles, to produce an ion-exchanged organoclay sample. A surfactant-stabilized palladium hydrosol was then mixed with this sample. No Pd particle deposition was experienced in this case. Such blank experiments furnish indirect evidence that the surfactant ions are (partially) desorbed from the protecting layer around the Pd particles and that these organic ions participate in the ion-exchange process with the native clay, an important step in the formation of the Pd-organoclay material. The basal spacings of the Pd−MM and Pd−HT materials were on average 1.93 and 2.77 nm, respectively, values only slightly higher than those for the corresponding organoclays in the absence of Pd particles.[1,41] Nevertheless, the half-height peak-widths in the XRD spectra were broadened as compared with the Pd-free organoclays. These observations, together with the TEM images, suggest that regular intercalation of the Pd particles between discrete clay layers is unlikely; the Pd particles are adsorbed to

external rather than to internal surface sites of the organoclays. The size distributions of the Pd particles (determined by TEM) are displayed in Figure 3 in the sequence Pd−MM1, Pd−MM2, Pd−HT1, and Pd−HT2. The monodisperse microstructure of the colloidal metal sol was retained in the catalysts: there was no appreciable difference between the size distributions of the Pd particles before and after deposition on the clay hosts. Furthermore, the Pd particles strongly adhered to the clay surface and were not leached out during application. A representative electron micrograph is displayed in Figure 4 for Pd−HT1, which indicates a random 2D spatial (surfacial) distribution and a fairly uniform size distribution of the Pd particles on the underlying HT lamellae. Agglomeration of the Pd clusters is seen to be absent.

We suggest that the basic principles of the above preparation technology are more general; the method can be adapted for the synthesis of various sorts of nanoparticles, stabilized by anionic or cationic surfactants, on a variety of oppositely charged ion-exchanger supports. Although the surface properties of the ion-exchanger materials undergo dramatic changes in consequence of the organophilization, the change in surface polarity can be a further advantage in catalytic applications, since a majority of liquid-phase hydrogenation reactions are conducted in nonaqueous media. Under these circumstances, organoclays may undergo swelling and disaggregation, as shown schematically in Figure 5, so that the catalytically active sites become more easily accessible for the reactant molecules.

Catalytic Test Reactions. *Activities.* The catalytic activity of a hydrogenation catalyst can be quantified in terms of r_i, the initial rate of hydrogenation of the alkene selected for the catalytic probe.[14,18,19,23−25] The value of r_i provides the initial rate of hydrogen uptake (milliliters per minute) per unit mass of the metal catalyst (grams of Pd). At a given value of the ratio S:C, continuous monitoring of the hydrogen consumption vs the duration of hydrogenation allows construction of the conversion plot (transformation of the alkene probe to the alkane). GC−MS analysis at intermediate stages indicated that the hydrogenation reaction hex-1-ene → hexane was accompanied by the consecutive (isomerization plus hydrogenation) reactions hex-1-ene → (*trans*-hex-2-ene; *cis*-hex-2-ene) → hexane. The conversions of styrene to ethylbenzene, cyclohexene to cyclohexane, and hex-1-ene to hexane are plotted against time in Figure 6 for the Pd−HT1 catalyst. Qualitatively, similar plots were obtained for the other catalyst samples. The r_i values were calculated from the initial slope of the conversion vs time plots. Assuming spherical morphology and a mean particle diameter d, the apparent dispersion of the metal, e.g., the number of surface Pd atoms (Pd_s) relative to the number of total (surface plus bulk) Pd atoms, can be estimated as $D = Pd_s/Pd = 0.6/d$.[42] If r_i and D are known quantities, the activity of the catalyst is best described in terms of the turnover frequency, TOF. The apparent TOF provides the number of alkene molecules transformed to alkane molecules per second per surface Pd atom. The apparent TOFs for the hydrogenations of the three alkenes on the four Pd-organoclay catalysts are given in Table 1 and Figure 7. For comparison, the r_i values of some Pd−MM catalysts, reported in the literature, were converted to TOFs, and the results are also indicated in Figure 7. Although the structures of these catalysts differ in some respects from the structures of Pd−MM and Pd−HT, they are closely related to the present catalysts in terms of
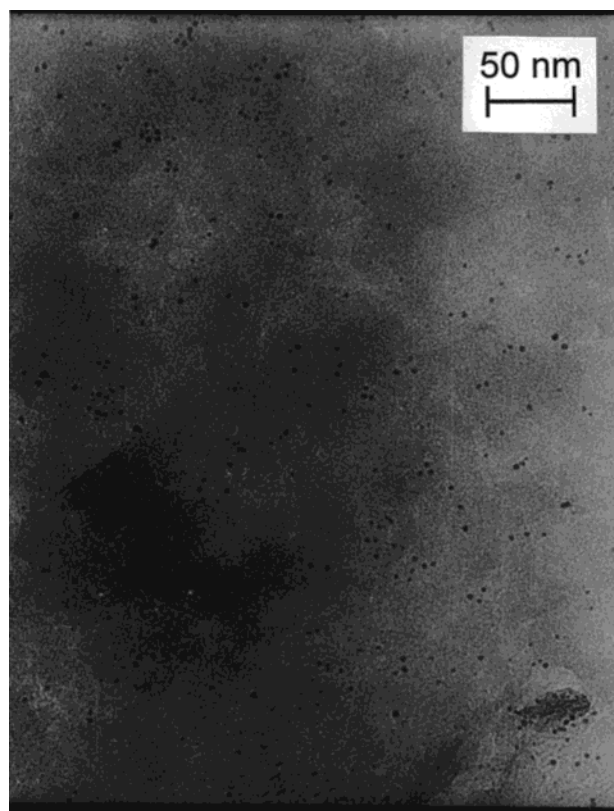
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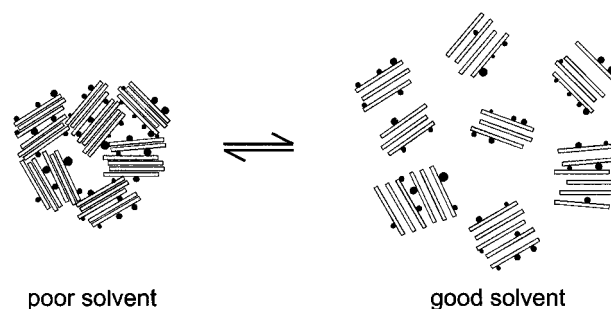(42) Aben, P. C. *J. Catal.* **1968**, *10*, 224.
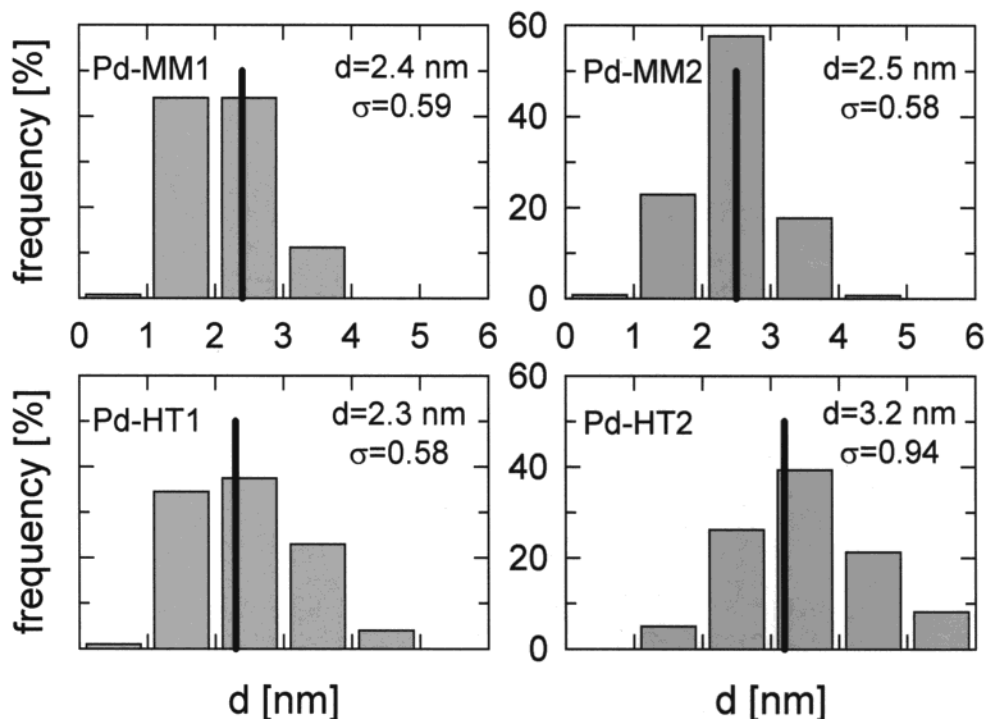
Figure 3. Size distributions of Pd particles on Pd-organoclay materials determined from TEM images.

**Figure 4.** Transmission electron micrograph of Pd−HT1 (0.10 wt % Pd; d = 2.3 nm).

Figure 5. Microstructure of Pd-organoclay materials in poor and good solvents. Disaggregation and swelling facilitate catalytic applications. Surface-bound alkyl chains are omitted for clarity.

their composition. The palladium-phosphinated−montmorillonite (Pd-phos−MM) catalyst of Choudary et al.[14] is a heterogenized, homogeneous catalyst; the Pd−MM catalysts of Crocker et al. (Pd-pill−MM)[18] are hydrophilic, intercalation catalysts in which the Pd clusters are mostly situated in the clay galleries, resembling the structure of classical pillared clays. It may be noted that, to reach a relatively high conversion in a reasonable experimental time (e.g., less than 1 h), the ratios S:C for the Pd−MM and Pd−HT catalysts were chosen to be 2000:1, as compared to 500:1 for Pd-pill−MMs and 100:1 for Pd-phos−MM; the higher ratio implies a higher catalytic activity on the same time scale of the experiments. The following statements can be made on the basis of Figure 7.

(i) The activities of the present Pd−MM and Pd−HT catalysts are superior to or comparable with those of the previously reported Pd−MM catalysts. The hydrogenation activities of the catalysts increase in the sequence Pd-phos−MM < Pd-pill−MM ≈ Pd−HT < Pd−MM. The very high activities of Pd−MM and Pd−HT may be related to the strongly hydrophobic character of these catalysts, which implies good wetting, disaggregation, and swelling in toluene (see Figure 5).

(ii) In general, the apparent TOF increases in the sequence cyclohexene < hex-1-ene < styrene, irrespective of the nature of the Pd catalyst (or the support). This observation may be related to the position of the olefin bond in the probe molecules. Hex-1-ene is a terminal olefin, which is more easily hydrogenated than cyclohexene by the Pd species, being that cyclohexene is an internal olefin. Styrene is a terminal olefin in which the C═C double bond is in conjugation with the aromatic benzene ring; this
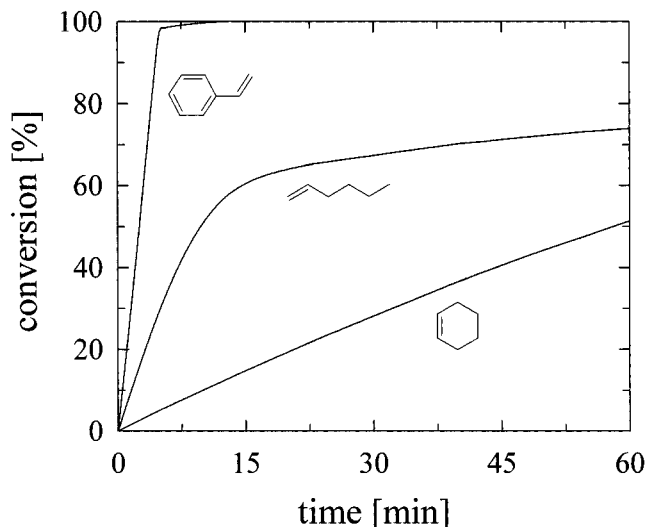
Figure 6. Conversion plots of the hydrogenation of alkenes to alkanes by the catalyst Pd−HT1 (solvent, 1 mL of toluene; substrate, 0.1 mL of styrene, hex-1-ene, or cyclohexene; S:C = 2000; $p = 1$ atm; $T = 298$ K).
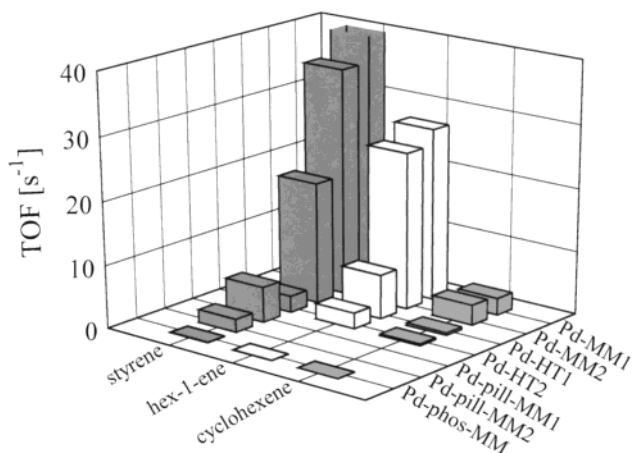
Figure 7. Apparent TOF values for the hydrogenations of styrene, hex-1-ene, and cyclohexene by Pd-organoclay catalysts in comparison with a heterogenized homogeneous catalyst (Pd-phos−MM)[14] and hydrophilic, (partially) pillared clays (Pd-pill−MMs).[18]

conjugated structure accounts for the higher reactivity than that of the single terminal olefin hex-1-ene.

(iii) The Pd−MMs are more active than the Pd−HT catalysts; this may be related to the difference in colloidal behavior between the two supports; the wetting, disaggregation, and swelling properties of C_{14}−MM in toluene are better than those of C_{12}−HT in the same solvent (Figure 5).

(iv) The catalytic activity (in terms of TOF) increases with a decrease in Pd particle size and Pd loading (structure-sensitive reaction). This pecularity has recently been explained by dividing the total number of surface Pd atoms, Pd_s, into terrace sites and defect sites, the latter being the real active centers for catalysis in Heck coupling reactions.[43] Such an analysis for the hydrogenation of olefinic bonds is beyond the scope of the present study (a series of Pd-organoclay catalysts is required, differing in the Pd particle size) but would certainly be beneficial in future studies. Furthermore, the Pd particles may form bridges between the clay lamellae, thereby reducing the

number of surface sites accessible for the reactant molecules.[22] Because the present apparent TOF values may be regarded as the initial reaction rates normalized with respect to Pd_s, the dependence of the TOF on the particle size and metal loading indicates that the surface Pd atoms do not all possess equal reactivity and accessibility in the above reactions. The catalytic activity may be further influenced by the surface properties of the support.

Selectivities. Although Pd is the best metal catalyst for the highly selective semihydrogenation of acetylenic bonds to olefinic bonds,[44−47] a low percentage of overhydrogenation to saturated hydrocarbons does occur even with the best catalysts. Bond selectivity can be improved with certain additives, which render the Pd surface sites less active concerning olefin hydrogenation, whereas the efficiency for acetylene (half) hydrogenation is retained.[44,46] The bond selectivity can also be improved by increasing the dispersion of the metal.[45,47] Pd is capable of absorbing hydrogen under mild conditions (at ambient temperature and low pressure) to produce the α- and β-hydride phases, two interstitial solid solutions,[48] which may furnish alkene admolecules with sufficient hydrogen to transform them into the corresponding alkane molecules. Because ultrafine Pd particles ($d < 2-3$ nm) are too small to form the β-hydride phase,[45,47] alkene molecules can leave the active centers before overhydrogenation occurs.

Stereoselectivity is a further point of interest in the half-hydrogenation of alkynes. The associative adsorption mechanism[44] favors formation of the cis isomer, even if the trans configuration is the thermodynamically more stable state. In most cases, the addition of atomic hydrogens takes place from below the axis of unsaturation of the adsorbed species, resulting in formation of the *cis*-alkene; the *trans*-alkene is formed only if hydrogen addition occurs from above the axis of unsaturation.[44] In general, the cis isomer is the major product of the half-hydrogenation of alkynes on Pd surfaces. Nevertheless, various amounts of the *trans*-alkene are always formed, either as the initial product or as a result of subsequent isomerization.

The half-hydrogenation of 1-phenyl-1-pentyne was chosen as the selectivity probe for the present Pd-organoclay catalysts. The results for Pd−MM1, reported in a recent publication,[49] are reproduced here in a revised format to facilitate comparison with the results for Pd−HT1. The overall products of the hydrogenation reactions are 1-phenyl-*cis*-1-pentene, 1-phenyl-*trans*-1-pentene (the products of half-hydrogenation), and 1-phenylpentane (the product of overhydrogenation). The conversion C_H, the bond selectivity S_B, and the stereoselectivity S_S (each expressed in percent) are plotted against the reaction time in Figures 8 and 9 for Pd−MM1 and Pd−HT1, respectively. S_B is defined as the number of alkene molecules relative to the number of alkene plus alkane molecules. S_S is defined here as the number of cis isomer molecules relative to the total number of cis plus trans isomer molecules. The following statements can be made on the basis of Figures 8 and 9.

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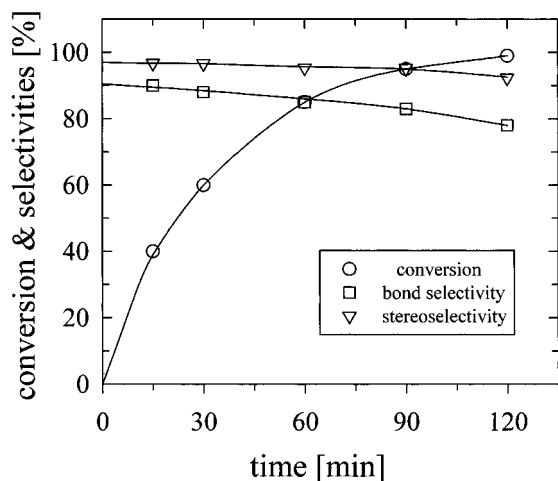
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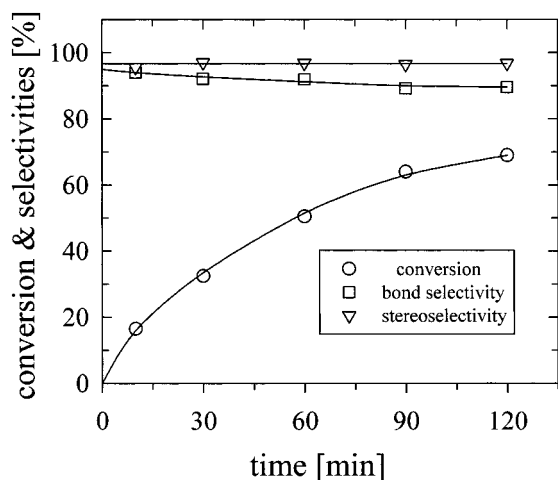
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Figure 8. Hydrogenation of 1-phenyl-1-pentyne by the catalyst Pd−MM1 (solvent, 1 mL of THF; catalyst, 5 mg; S:C = 7500; p = 1 atm; T = 298 K). C_H, conversion; S_B, bond selectivity; S_S, stereoselectivity; each expressed as a percent.

Figure 9. Hydrogenation of 1-phenyl-1-pentyne by the catalyst Pd−HT1 (solvent, 1 mL of THF; catalyst, 10 mg; S:C = 2500; p = 1 atm; T = 298 K). C_H, conversion; S_B, bond selectivity; S_S, stereoselectivity; each expressed as a percent.

(i) For Pd−MM1, C_H = 100% is reached at S:C = 7500 in 2 h; for Pd−HT1, C_H = 70% is reached at S:C = 2500 in 2 h. It follows that the activity of Pd−MM1 is higher than that of Pd−HT1. This is in accordance with what was reported in the previous section (Activities) under (iii).

(ii) For Pd−MM1, S_B decreases from 90 to 78%, and S_S decreases from 97 to 92% as C_H increases from 0 to 100%. For Pd−HT1, while S_B decreases from 94 to 90%, S_S remains apparently unchanged at 97% as C_H increases from 0 to 70%. This trend implies that better bond selectivity and stereoselectivity are obtained at lower conversions. Pd−HT1 proved to be a slightly more selective but less active catalyst than Pd−MM1. We cannot decide at present whether this difference can be attributed to the different history of the Pd particles (anionic or cationic surfactants being used as the stabilizing agents) or whether the selectivities were influenced by the nature of the support.

(iii) The bond selectivities and stereoselectivities of Pd−MM1 and Pd−HT1 in the half-hydrogenation of 1-phenyl-1-pentyne are similar to those of Pd−MMs in the half-hydrogenation of 1-phenyl-1-butyne[25] and to those of Pd-pill−MMs in the half-hydrogenation of 1-phenyl-1-propyne.[19]

(iv) The Lindlar catalyst Pd−L (Pd/CaCO$_3$, partially poisoned with lead[46]) is one of the best, commercially available, selective hydrogenation catalysts.[25,44,49] The activities of the present Pd-organoclay catalysts well exceeded that of Pd−L, which was used at S:C = 500 to achieve C_H = 32% in 30 min but otherwise under the same experimental conditions as in the present study.[49] The stereoselectivities of the Pd-organoclay catalysts are essentially the same as that of the Pd−L catalyst for which S_S = 97% was reported at C_H = 32%.[49]

In summary, the Pd-organoclay materials described in the present study proved to be very efficient hydrogenation catalysts; they are superior in activity and competitive in selectivity relative to the closely related Pd catalysts described in earlier studies.

Conclusions

The reduction of Pd(acac)$_2$ with hydrazine in the presence of the amphiphile MTA$^+$Br$^-$ or Na$^+$DS$^-$ afforded highly dispersed metallic Pd particles surrounded by a protective adsorption layer of the anionic or cationic surfactant. When the palladium hydrosols stabilized by MTA$^+$Br$^-$ or Na$^+$DS$^-$ were mixed with aqueous suspensions of Na$^+$MM$^-$ or hydrotalcite nitrate (HT$^+$NO$_3^-$), respectively, the ion-exchange reaction between the stabilizing surfactant ions and the counterions of the oppositely charged clay particles resulted in the formation of the low-loaded, hydrophobic Pd-clay materials Pd−MM and Pd−HT. The Pd-organoclays can readily be dispersed in nonaqueous solvents in which the platelike particles undergo disaggregation and swelling. Liquid-phase catalytic hydrogenation reactions were performed to test the activities and selectivities of the Pd-organoclay materials. Both Pd−MM and Pd−HT exhibited high catalytic activities in the hydrogenations of styrene, hex-1-ene, and cyclohexene. The catalysts displayed high bond selectivity and stereoselectivity in the partial hydrogenation of 1-phenyl-1-pentyne to the *cis*-alkene. The activity and selectivity of these novel materials are higher than or comparable to those previously reported for some closely related Pd catalysts. Further advantages of the present Pd-organoclay materials are the simplicity and the low cost of the preparation. It is anticipated that the basic principles of the preparation methodology described in this study can readily be extended to the preparation of a variety of nanoparticles stabilized by ionic surfactants on a variety of oppositely charged ion-exchanger supports.