Synthesis and Characterization of Palladium Crystallites Intercalated in Montmorillonite

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Reduction of electrophilic Pd(II) complexes intercalated in montmorillonite under mild conditions (0 °C in MeOH) has been shown to afford highly dispersed metallic palladium, located mainly in the interlamellar regions of the clay. Transmission electron microscopy reveals an unusual platelet morphology for the interlamellar metal particles, suggesting that the clay structure may impose a kinetic constraint on the attainment of a thermodynamically more favorable spherical morphology.

Smectite clays such as montmorillonite have in recent years attracted interest as supports for metal and metal complex catalysts. These minerals, which are layered lattice silicates, can be readily functionalized, either via ion exchange with a positively charged metal complex or with organic ligands to which a metal can subsequently be attached.[1] Furthermore, clays possess certain physical and chemical properties which potentially permit modification of the selectivity and activity of supported catalysts. Principal among these properties is the laminar structure of clays, theoretically enabling selective substrate adsorption based on size or shape (i.e., a molecular sieving effect). Additionally, there exists the potential that transition-state selectivity may arise in reactions occurring in the sterically restricted interlamellar regions.

Recent studies concerning the hydrogenation of unsaturated substrates by interlamellar metal complex catalysts have indeed provided a number of examples of these features.[1,2] To date there have been fewer reports concerning the preparation and catalytic properties of metal particles dispersed on swelling clay supports,[3] although the use of noble metal-containing pillared clays and synthetic mica–montmorillonite clays for hydrocracking, hydroisomerization, and Fischer–Tropsch reactions has been reported.[4] In the present paper we describe the preparation, under very mild conditions, of highly dispersed palladium in the interlamellar region of montmorillonite clay, together with observations concerning the morphology and catalytic properties of the interlamellar metal particles.

For the purposes of this study samples were prepared by ion-exchanging sodium montmorillonite[5] (hereafter designated as MM-Na^+) with the Pd(II) complexes $[Pd(L)_{4-x}(L')_x][BF_4]_2$ (L = MeCN, L′ = PPh_3, $x = 1$ or 0)[6] in the manner described previously for the related complex $[Pd(PPh_3)_3(NCMe)]^{2+}$:[7]

$$\mathrm{MM\text{-}2Na^+ + [Pd(L)_{4-x}(L')_x][BF_4]_2 \rightarrow MM\text{-}[Pd(L)_{4-x}(L')_x]^{2+} + 2NaBF_4} \quad (1)$$

Intercalation of the complexes was confirmed by X-ray powder diffraction, the basal spacing of the clay increasing from 9.6 Å (for vacuum-dried MM-Na^+) to 12.6 and 15.8 Å for the products obtained with $[Pd(NCMe)_4]^{2+}$ and $[Pd(PPh_3)(NCMe)_3]^{2+}$, respectively. The magnitudes of these spacings are consistent with an orientation in which the metal–ligand bonds of the intercalated complexes lie parallel to the silicate sheets, the palladium d_{z^2} orbital being perpendicular to the *ab* plane.

Reduction of the intercalated complexes was accomplished by suspending the clays in methanol at 0 °C for 30 min:

$$\mathrm{[Pd(L)_{4-x}(L')_x]^{2+} + CH_3OH \rightarrow Pd^0 + CH_2{=}O + 2H^+ + (4-x)L + xL'} \quad (2)$$

$Pd_{5/2}$ binding energies determined from XPS spectra confirm the formation of palladium metal in the product materials (Table I), while comparison of surface and bulk

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(5) The approximate anhydrous unit cell formula determined on the basis of elemental analysis and ^{27}Al NMR MAS spectroscopy was $Na_{0.62}[Al_{3.16}Fe^{III}_{0.36}Fe^{II}_{0.08}Mg_{0.40}](Si_{7.86}Al_{0.14})O_{20}(OH)_4$; the measured cation exchange capacity was 82 mequiv/100 g. The MM–Na^+ was obtained by purification of bentonite (BDH) using a standard procedure: van Olphen, H. *An Introduction to Clay Colloid Chemistry*; Wiley-Interscience: New York, 1977; pp 249–252.

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Figure 1. Transmission electron micrograph of 1. Folding of the clay layers (through ca. 90°) at the clay particle edge is apparent.

Table I. Pd $3d_{5/2}$ Binding Energies for MM–Na^+/Pd and Related Materials

solid	BE[a] (eV)	ref
MM–Na^+/$[Pd(NCMe)_4]^{2+}$	337.9	this work
MM–Na^+/Pd (1)	335.7	this work
MM–Na^+/$[Pd(PPh_3)(NCMe)_3]^{2+}$	337.5	this work
MM–Na^+/Pd (2)	336.0	this work
Pd/SiO_2	335.6	12, 13
	335.1–335.4	14
Pd/Al_2O_3	335.7	13
	334.9–335.0	15
metallic Pd	334.9–335.6	12–15

[a] Binding energies for this work are referenced to C 1s (284.6 eV).

palladium concentrations determined by XPS and elemental analysis (WDX), respectively, indicates that the palladium is homogeneously dispersed throughout the clay particles.

The facile manner in which these highly electrophilic Pd(II) complexes undergo reduction in methanol may be rationalized in terms of a mechanism in which methoxide-ion attack on the starting complex generates a $Pd^+–OCH_3$ species; hydrogen transfer to the metal[8] with concomitant liberation of CH_2O would then generate a $Pd^+–H$ species, which upon proton loss would afford zerovalent palladium. The ease with which many late transition-metal alkoxide complexes undergo hydrogen-transfer reactions suggests[8] that this methodology could find more general application in the preparation of supported metals.

To gain an insight into the form and location of the palladium particles present, a TEM analysis was performed on reduced MM–Na^+/$[Pd(NCMe)_4]^{2+}$ (**1**) and MM–Na^+/$[Pd(PPh_3)(NCMe)_3]^{2+}$ (**2**) samples having Pd loadings of 1.0 and 2.2 wt %, respectively. Considering first 1, particularly noteworthy is the finding that the palladium in this material is present as particles of platelet or raftlike morphology, with their widths being typically a factor of 3 smaller than their diameters measured along the longest axis. Selected area electron diffraction of a collection of the particles within the clay confirmed their composition as metallic palladium. In interpreting the evidence for the palladium particle morphology, it is important to realize that the clay particles are oriented preferentially with their basal planes coplanar with the carbon film support. This conformation is illustrated in Figure 1, in which folding of the clay planes at the edges of the clay particles is also apparent; when the angle of folding approaches 90° the individual clay planes are resolved.

The evidence for the interpretation of palladium particle shape is based on the following observations:

(a) Several palladium particles were imaged "edge-on" and appeared elongated within the clay matrix. To accommodate the particles, the clay planes were considerably distorted, as shown in Figure 2. This type of local distortion was distinct from the more macroscopic phenomenon of plane cleavage.

(b) The total palladium particle contrast, arising from both diffraction and amplitude contrast mechanisms, was in agreement with a platelet morphology; thus when the electron beam passed through the particles in an orientation perpendicular to the clay planes, particle contrast was low. However, when the beam had to travel the length of the particle (i.e., parallel to the clay sheets), the

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(8) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 90.

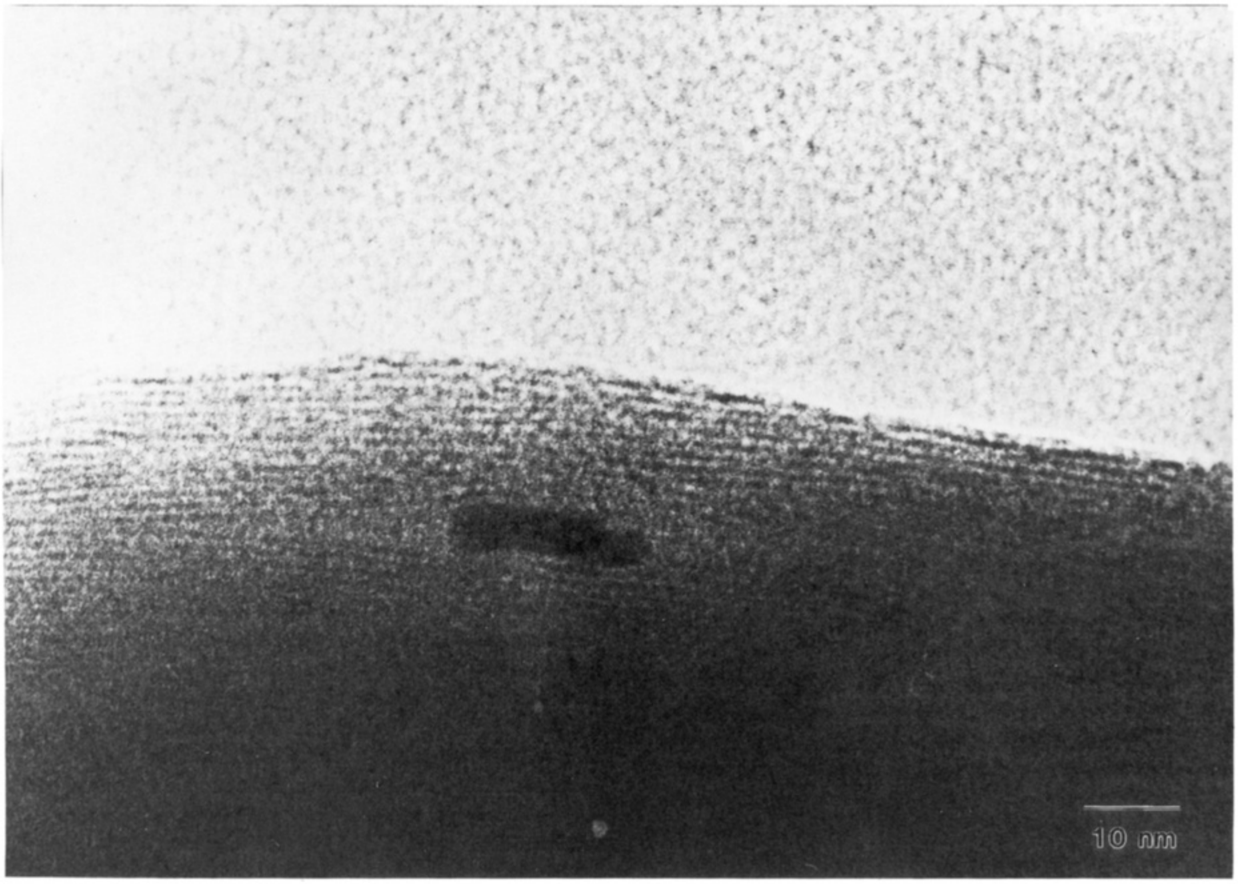

Figure 2. Transmission electron micrograph of 1. Clearly visible is the elongated form of the palladium particle and the distortion of the surrounding clay layers.

scattering was stronger and hence the particle showed higher contrast.

(c) When viewed from a direction approximately perpendicular to the clay planes, it was apparent that the particles were of irregular morphology as shown in Figure 3.

The observation of a nonspherical form for the palladium particles indicates that particle morphology is strongly influenced by the presence of the layered clay structure. Indeed it can be speculated that the particles may be kinetically inhibited from developing a more spherical morphology (thermodynamically more stable due to the minimisation of surface free energy) by the constraints imposed by the silicate sheets. Additionally, the possibility that the palladium particles may be stabilised with respect to a more spherical morphology as a consequence of interactions with the clay surface (a thermodynamic effect) cannot be discounted.[9]

For the reduced MM–Na$^+$/[Pd(PPh$_3$)(NCMe)$_3$]$^{2+}$ material (**2**) no conclusions can be drawn regarding the morphology of the palladium crystallites present owing to their small size (median particle diameter = 20–30 Å), although the few larger particles observed appeared to be nonspherical. Note that the palladium in this solid is more highly dispersed than in 1, for which a median particle diameter of 90–120 Å was found. Since both materials were reduced under identical conditions, these findings graphically illustrate the important role that the nature of the precursor Pd(II) complex (and its associated reduction behavior) can play in determining the degree of dispersion of the supported metal.

For both samples it can be concluded that the particles are located principally between the clay layers. Significant aggregation of the palladium particles at the sheet edges was not observed for either sample, while for **1** only the platelet morphology was observed. Additionally, for **2**, X-ray powder diffraction revealed a slight increase in the basal spacing of the clay after reduction of the palladium complex, corresponding to an interlayer spacing of 6.4 Å. While this observation is consistent with the presence of palladium particles in the interlayer regions of the clay, it should be noted that this interlayer spacing is rather smaller than the median particle diameter of 20–30 Å determined by TEM, a result which can explained on the basis of a platelet morphology for the particles. Materials prepared at lower palladium loadings gave diffractograms which were rather uninformative, the broad d_{001} reflections (observed both before and after reduction) being indicative of a less ordered structure.

These findings contrast with previous observations concerning the preparation of dispersed platinum on montmorillonite via reduction of intercalated Pt(II) complexes.[3d] TEM analysis of samples reduced in hydrogen at 140 °C (for a minimum of 9 h) revealed that reduction was accompanied by a collective migration of platinum atoms and/or crystallites from the external surface of the clay to sites of low negative charge on the external surfaces and edges. A number of possible

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(9) However, the large difference in binding energies between the palladium 4d and oxygen 2p orbitals suggests that metal–substrate interactions should be rather weak: Mason, M. G. *Phys. Rev. B* **1983**, *27*, 748. We also note that the Pd 3d$_{5/2}$ binding energy of 335.7 eV observed for reduced MM–Na$^+$/[Pd(NCMe)$_4$]$^{2+}$ shows reasonable agreement with the values typically reported for both metallic palladium and palladium supported on silica (see Table I).

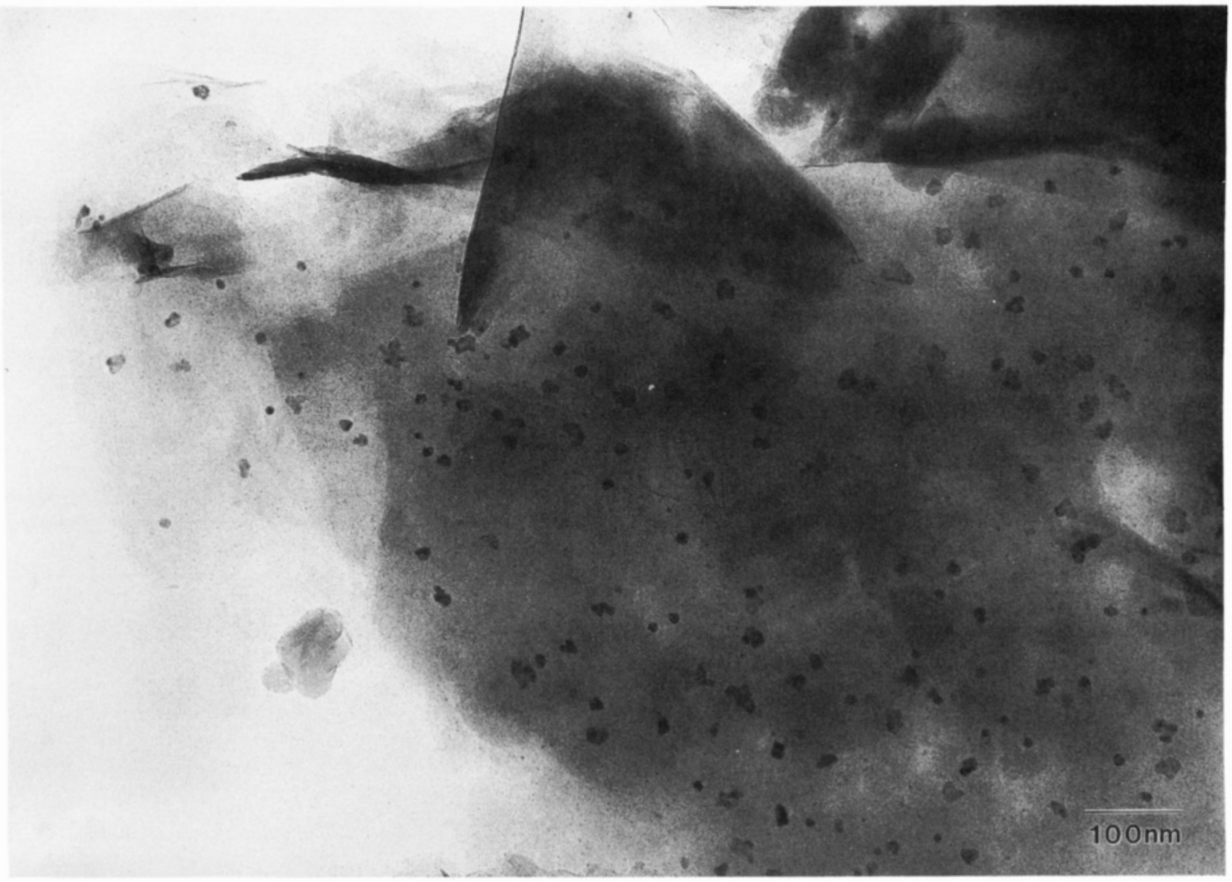

Figure 3. Transmission electron micrograph of **1** showing irregular particle morphology.

Table II. Hydrogenation Activity of Selected Palladium Catalysts[a]

catalyst	substrate	product	initial rate (mL of H_2/(mmol of Pd min))	conversion[b,c] (%)	selectivity[c] (%)
1	$PhCH{=}CH_2$	$PhCH_2CH_3$	351		
2	$PhCH{=}CH_2$	$PhCH_2CH_3$	448		
Pd/SiO_2 (1%)[d]	$PhCH{=}CH_2$	$PhCH_2CH_3$	302		
1	$PhC{\equiv}CCH_3$	(*Z*)-$PhCH{=}CHCH_3$	365	87.1	81.2
2	$PhC{\equiv}CCH_3$	(*Z*)-$PhCH{=}CHCH_3$	589	97.3	85.1
Pd/Al_2O_3 (1%)[e]	$PhC{\equiv}CCH_3$	(*Z*)-$PhCH{=}CHCH_3$	601	93.8	81.1

[a] Conditions: temperature, 18 °C; $P(H_2)$, 1 atm; solvent, methanol, 20 mL; Pd, 0.03 mmol; substrate, 15.0 mmol. [b] Conversion of 1-phenylpropyne after uptake of 1.0 equiv of H_2. [c] Determined by GLC (HP-1 cross-linked dimethylsilicone column, ethylbenzene as internal standard). [d] Reduced $[Pd(PPh_3)(NCMe)_3][BF_4]_2/SiO_2$. [e] Obtained from Aldrich Chemical Co.

explanations could account for the differing behavior of the metal particles prepared in the previous[3d] and present work. First, the lower reduction temperature employed in the current work should result in decreased thermal migration of metal atoms and crystallites. Second, from a thermodynamic viewpoint the presence of metal particles between the clay sheets should be less disfavored in the present case due to the lower negative charge on the silicate sheets of the clay employed (0.6 e/unit cell versus 0.9 e/unit cell for the montmorillonite employed in ref 3d, as calculated from the respective unit cell formulas), resulting in a comparative reduction in electronic repulsion between the substrate and metal particles. Additionally, it should be noted that the surface free energy of palladium is intrinsically lower than that of platinum (as reflected in their respective heats of vaporization),[10] although in the presence of adsorbates such as hydrogen or methanol this may no longer hold.

First results show that the interlamellar palladium nanoparticles constitute highly active catalysts for the hydrogenation of alkenes and alkynes (Table II). Styrene is readily hydrogenated to ethylbenzene in the presence of **1** or **2** suspended in methanol, indicating that the nanoparticles are readily accessible to sterically undemanding substrates.[11] In comparison, a 1% Pd/SiO_2 catalyst, prepared by methanol reduction of $[Pd(PPh_3)(NCMe)_3][BF_4]_2$ in the presence of Aerosil (BET area = 178 m^2/g), showed slightly lower activity. 1-Phenylpropyne is also hydrogenated by the clay-based catalysts at high rates and with good selectivity to the *cis*-alkene. Thus reaction of the alkyne with 1.0 equiv of hydrogen in the presence of **2** led to the formation of (*Z*)-$PhCH{=}CHCH_3$ with a selectivity of 85.1%, the other products comprising the *trans*-alkene (3.9%) and the alkane (11.0%).

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(10) Miedema, A. R. *Z. Metallkd.* **1978**, *69*, 287.

(11) In the case of bulkier substrates, molecular sieving effects are observed: Crocker, M.; Herold, R. H. M.; Buglass, J. G.; Companje, P., submitted to *J. Catal.*

(12) Pitchon, V.; Guenin, M.; Praliaud, H. *Appl. Catal.* **1990**, *63*, 333.

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(14) Fleisch, T. H.; Hicks, R. F.; Bell, A. T. *J. Catal.* **1984**, *87*, 398.

(15) Shyu, J. Z.; Otto, K.; Watkins, W. L. H.; Graham, G. W.; Belitz, R. K.; Gandhi, H. S. *J. Catal.* **1988**, *114*, 23.

In summary, low-temperature (0 °C) reduction of electrophilic Pd(II) complexes intercalated in montmorillonite has been shown to afford highly dispersed metallic palladium, located mainly in the interlamellar regions of the clay. An unusual platelet morphology has been observed for the interlamellar metal particles, suggesting that the clay structure imposes a kinetic constraint on the attainment of the more thermodynamically favored spherical particle morphology. Initial results indicate that these materials possess excellent hydrogenation activity.

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