A Novel 'Anchored' Palladium(II) Phosphinated Montmorillonite: the First Example in the Interlamellars of Smectite Clay

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Montmorillonite containing $PdCl_2$ anchored *via* pendant phosphinated groups in the interlamellar region has been synthesized, characterized, and found to hydrogenate terminal alkenes and alkynes selectively.

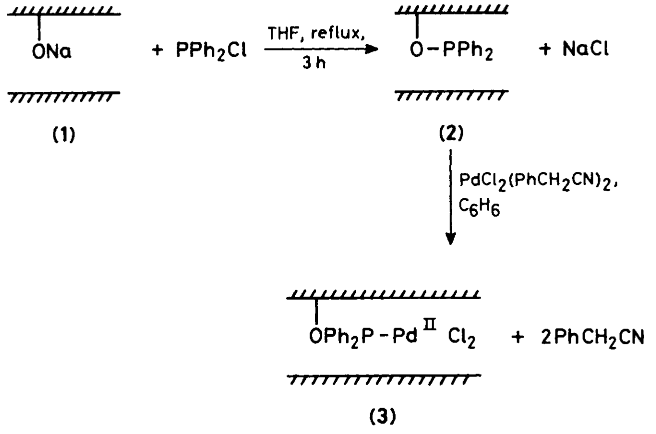
The swelling type of silicates such as montmorillonite and hectorite were recently employed for immobilization of cationic transition-metal complexes and used as catalysts for hydrogenations and hydroformylations.[1,2] Montmorillonite is known to participate in Friedel–Crafts reactions, esterification, and etherification to form stable covalently bonded organic moieties in the interlamellar region.[3] We now report the synthesis and characterization of the first example of a montmorillonite with palladium(II)-phosphine units 'truly anchored' in the interlamellars.

Vacuum-dried sodium montmorillonite (**1**) (5 g) was refluxed with chlorodiphenylphosphine (13 cm^3) in dry tetrahydrofuran (THF) for 3 h under nitrogen and then filtered and washed thoroughly to give the phosphinated montmorillonite (**2**), which in turn was shaken with solutions of varying amounts of $PdCl_2(PhCH_2CN)_2$ in dry benzene at room temperature under nitrogen until the colour of the Pd complex disappeared (2—3 h) to give the brown $PdCl_2$-anchored phosphinated montmorillonites (**3A**—**C**) (Scheme 1). The powder *X*-ray diffraction patterns of (**2**) and (**3**) showed basal region expansion to 14.5 and 15.2 Å respectively from the 9.4 Å of dehydrated (**1**). These results indicate the presence of an organic moiety in the interlamellar region.

The *X*-ray photoelectron spectra (x.p.s.) for palladium in the catalysts with different metal content (**3A**—**C**) and in the used catalyst (**3C**) show well resolved spin doublets (Figure 1). The P, Pd, and Cl atomic ratio determined by x.p.s. agrees well with the analytical data; the suitability of this technique for quantitative analysis of montmorillonites has recently been reported.[4] In addition to the empirical atomic ratio of Pd to Cl (1:2), the binding energies (E_b) of the palladium $3d_{5/2}$ level (338.40—338.46 eV) and its full width at half maximum ($\Delta_{1/2}$) indicate that the palladium in the catalysts is in the divalent state (Table 1). However, a small shoulder at lower binding energies (336.0 eV), which coincides with that for 5% commercial palladium on carbon, strongly suggests formation of small quantities of Pd^0 (Figure 1). The E_b values for phosphorus in compound (**2**) correspond to the trivalent state, and no change in E_b is observed even after complexation to give (**3**) owing to its strong π-acceptor nature.

Compounds (**2**) and (**3**) exhibit an aromatic C=C stretching i.r. band at 1440 cm^{-1}, and (**3**) shows a peak at 350 cm^{-1} (Pd–Cl).[5] The foregoing analytical, *X*-ray diffraction, and x.p.s. evidence indicates the three-co-ordinate structure (**3**) in the interlamellar region for the complexes.

Catalyst (**3C**) is more active for the hydrogenation of alkenes and alkynes than the analogous polymer-anchored Pd^{II} catalyst under identical conditions[6] (Table 2) and the enhanced activity may be attributed to the change in the electronic environment around palladium in the complex. Catalyst (**3C**) selectively hydrogenated terminal alkenes (Table 2, entries 1, 2, and 4). The terminal alkyne, phenylacetylene (entry 9), was hydrogenated completely to yield styrene selectively. All reactions proceeded quantitatively.



Scheme 1

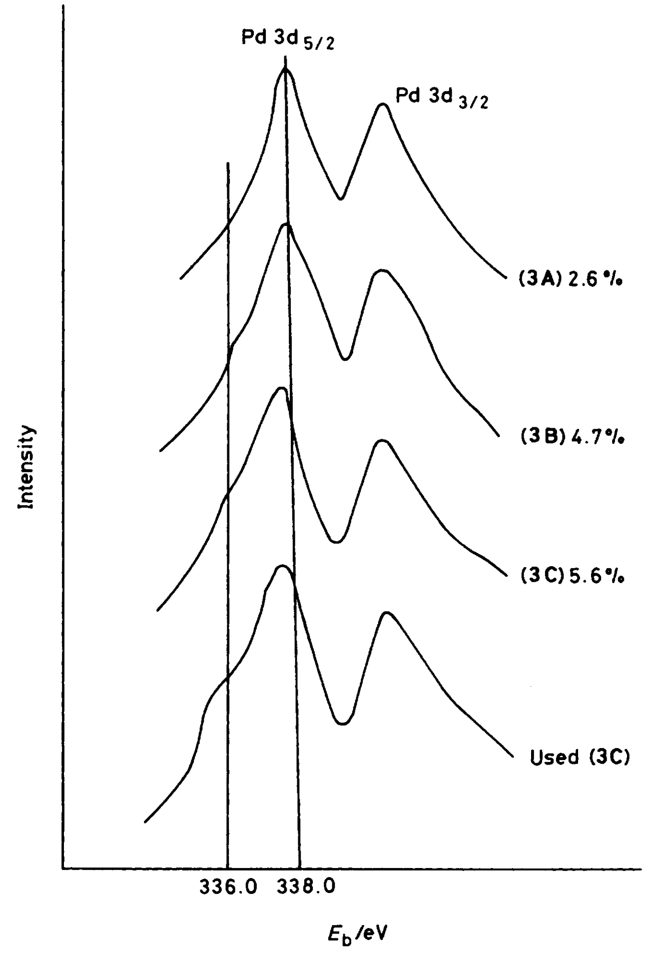


Figure 1. X.p.s. of (**3A**—**C**).

Table 1. X.p.s. results for Pd $3d_{5/2}$, Cl 2p, and P 2p.[a]

	Electron binding energy with f.w.h.m. ($\Delta_{1/2}$)			
Compound	Pd $3d_{5/2}$	$\Delta_{1/2}$	Cl 2p	P 2p
5% Pd/C	336.4	3.2	—	—
$PdCl_2$	338.0	1.9	199.56	—
$PdCl_2(PPh_3)_2$	338.0	2.2	199.54	—
$PdCl_2(PhCH_2CN)_2$	338.7	2.0	199.46	—
(2)	—	—	—	131.8
(3A)	338.40	2.1	199.48	131.8
(3B)	338.44	2.2	199.51	131.9
(3C)	338.46	2.4	199.60	131.9
Used **(3C)**	338.56	2.6	199.71	131.9

[a] E_b for C 1s as standard (285.0 eV). E_b values ±0.2 eV.

Table 2. Comparison between activities of clay-bound **(3C)** and polymer-bound catalysts (initial H_2 uptake in ml/min).

Entry	Substrate	Clay-bound[a]	Polymer-bound[f]
1	Styrene	10.3	6.1
	Styrene	9.4[b]	7.7[b]
	Styrene	7.1[c]	6.1[c]
	Styrene	No reaction[d]	2.8[d]
	Styrene	Not studied[e]	8.1[e]
2	Hept-1-ene	4.5	3.9[e]
3	Hept-2-ene	No reaction	0.6
4	Hex-1-ene	3.6	–[g]
5	Hex-2-ene	No reaction	–[g]
6	Cyclohexene	3.3	0.8
7	Stilbene	No reaction	–[g]
8	Hex-3-yne	No reaction	–[g]
9	PhC≡CH	3.0	3.5
10	PhC≡CPh	No reaction	–[g]

[a] [Catalyst] 3.0 mM; [substrate] 300 mM; temp. 25 °C; $p(H_2)$ 1 atm; THF solvent (25 ml) unless otherwise noted. [b] EtOH solvent. [c] Acetone. [d] Benzene. [e] Benzene–EtOH (1:1). [f] Polystyrene–divinylbenzene (2%) bound PPh_2. [g] Initial H_2 uptake not recorded, although these reactions gave good yields.

The inertness of the internal double bond in alkenes (entries 3 and 5) and stilbene (entry 7) and the internal triple bond in hex-3-yne (entry 8) and diphenylacetylene (entry 10) may be ascribed to steric hindrance, as these substrates could not complex with the palladium in the interlamellar region owing to the expected larger van der Waals repulsions between the silicate layers and substituent groups in disubstituted alkenes and alkynes than in monosubstituted ones, in the desired perpendicular orientation of the substrate to the interlayers in the palladium complex.

The solvent affects the activity of the catalyst, the activity being in the order THF > ethyl alcohol > acetone, while in benzene essentially no reaction takes place in the hydrogenation of styrene; these results correspond with the swelling properties of montmorillonite in these solvents.[7]

Leaching of Pd^{II} was not observed during these reactions. Analogous Ru, Rh, and Os phosphinated montmorillonites are being studied. This work suggests that sterically hindered double and triple bonds could be selectively reduced by suitable control of interlayer expansion.

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