JOURNAL OF CATALYSIS **130**, 41–51 (1991)

Synthesis and Catalytic Activity in Selective Hydrogenation of Palladium Complexes Anchored in Montmorillonite[1]

B. M. CHOUDARY,[2] K. RAVI KUMAR, AND M. LAKSHMI KANTAM

Indian Institute of Chemical Technology, Hyderabad 500 007, India

Received January 10, 1990; revised November 20, 1990

Functional groups such as diphenylphosphine, triphenylphosphine, and 4-picoline have been intercalated in montmorillonite, a swelling smectite clay; subsequent complexation with palladium has led to syntheses of various interlamellar montmorillionite-anchored palladium(II) complexes. These montmorillonite ligands and their complexes are characterised by elemental analyses, IR, XRD, and ESCA. Diphenylphosphinomontmorillonite–palladium(II) complex (**4B**(ii), the best catalyst of the series for hydrogenation reactions, hydrogenated alkynes to alkenes and to alkanes selectively, yields are quantitative. The internal double bonds are also hydrogenated, but with decreased rate of activity. Catalyst **4B**(ii) has shown consistent activity for a number of recycles in the hydrogenation of styrene, and hex-1-ene. Used catalyst was also tested for hydrogenation activity with various organic reactants. The rate of hydrogen absorption is almost the same as that with fresh catalyst under identical conditions. These data indicate that transient homogeneous complex species formed in the pretreatment remain unchanged during the recycles. Catalyst **4B**(ii) hydrogenated mono and disubstitued alkynes and alkenes in ethanol. On the other hand, diphenylphosphinite–montmorillonite–palladium(II) complex (**2B**) selectively hydrogenated monosubstituted alkynes and alkenes only under identical conditions. Catalyst **2B**, with its lower initial interlamellar spacings, has induced size selectivity as evidenced in the selective hydrogenation of monosubstituted reactants only, because the preferred perpendicular orientation of the transient reactant–palladium complex formed with monosubstituted olefins in the interlayer spacings of montmorillonite requires a space smaller than that expected for disubstituted ones. Easy adjustment of interlayer spacings by the incorporation of complex moieties of different sizes in the interlayers makes montmorillonite a practical alternative to zeolites for inducing size selectivity.

1. INTRODUCTION

Although homogenous catalysts are desirable because of their high activity and selectivity, separation of homogeneous catalysts from the products of reaction and/or recovery of the catalysts are inherent problems associated with conventional soluble catalysts. Catalyst recovery can be ignored in small scale laboratory reactions, and in other cases, distillation can be used to separate volatile products from the catalyst. However, catalyst recovery is very important for economic and technological viability in large scale industries. Transition metal complexes have been heterogenised by anchoring onto polymer (*1*) and inorganic oxide supports (*2*) as a step toward solving the separation problem. Leaching of the metal has been prevalent in the anchored complexes containing coordinated bonds between the metal and the ligand bound to the support, because the metal decoordinated during catalytic reaction from the ligand bound to the surface of the support, such as polymers and inorganic oxides, enters into the liquid medium instantaneously and has little possibility of recoordination with the ligands bound on the solid support. The recent development of the class of anchored catalysts such as polymers with a phosphido linkage (*3*) or with a σ-bond (*4*) or a soluble and recoverable ethylene oligomer

---

[1] IICT Communication 2208.

[2] To whom correspondence should be addressed.

0021-9517/91 $3.00

(*5*) devised to combat the problem of precious metal leaching from the support is of current interest.

Encapsulation of cationic complexes in the interlamellar space of the smectite swellable clays montmorillonite and hectorite (*6–8*) as a consequence of this development could not solve precious metal leaching because the transient neutral complex obtained by proton dissociation can be easily desorbed from the interlayer regions of montmorillonite (*6*). Recently we described the covalent incorporation of phosphine groupings into the interlamellar regions of montmorillonite and their subsequent complexation with palladium salts as an alternative and general strategy designed to solve the precious metal leaching problem because covalently bound phosphines with montmorillonite could not be desorbed (*9–12*). It is also conceived that interlayer basal oxygens of the montmorillonite, which can act as polydentate centres with their lone pairs of electrons, hold the decoordinated metal within the interlayer region without diffusing out, thus enhancing the chances of metal recoordination with the phosphines and thereby minimising the metal leaching. Parallel to this, a similar synthesised palladium complex chemically anchored on hectorite by amine groups, exhibited shape selectivity in the hydrogenation of alkenes (*13, 14*).

In the present paper, we describe in detail the synthesis and characterization of several functionalised montmorillonites and their palladium complexes; we also report on their reactivity in hydrogenation of alkynes and alkenes and on the continuous use of the catalyst for a number of recycles with a consistent rate of activity.

2. EXPERIMENTAL

2.1. Materials

Air and moisture-sensitive reactions were carried out with the use of standard inert atmosphere techniques; transfer and filtration of compounds were carried out using Schlenk vessels (*15*). Tetrahydrofuran (THF) was dried and deoxygenated by distilling over sodium–benzophenone in nitrogen atmosphere. Dry benzene was obtained by distilling over sodium. All the compounds were stored in nitrogen atmosphere.

Montmorillonite employed in the synthesis was obtained from the Clay Mineral Society or Fluka. Prior to use, the mineral was suspended as 1% weight slurry and was allowed to sediment for 24 h to remove denser impurities such as quartz and calcite.

2.2. Procedure

Preparation of functionalised montmorillonite. Na–montmorillonite (**1A**) was prepared starting from natural montmorillonite by the procedure of Posner and Quirk (*16*) where as H^+–montmorillonite (**1B**) was prepared according to the procedure of Spencer and Gieseking (*17*). Clays **1A** and **1B** were separated by centrifuge and washed free of chloride by deionized distilled water and vacuum dried at 80°C for 6 h to remove water. The traces of interlayer water were further removed by washing with dry ethanol followed by drying under suction (*18*).

Preparation of diphenylphosphinite–montmorillonite (**2A**). A 5-g quantity of **1A** in THF (10 ml) was taken in a three-necked 250-ml round-bottomed flask equipped with a N_2 inlet, a reflux condenser, and a pressure equalising funnel. Excess PPh_2Cl (13 ml, 70 mmol) in THF was added dropwise over a period of 10 min, with constant stirring. The reaction mixture was then refluxed at 70°C for 3 h cooled, and filtered under nitrogen atmosphere. The residue was thoroughly washed with benzene (20 ml) followed by methanol, ethanol, ethanol + water, acetone, THF, and benzene.

Preparation of chloromontmorillonite (**3**). H^+–montmorillonite (10 g) was treated with excess of freshly distilled $SOCl_2$ (100 ml) in dry benzene (100 ml) at reflux temperature for 24 h in an inert atmosphere in a 500-ml RB flask. Subsequently, it was filtered and washed thoroughly under inert atmosphere (in a glove box) and dried (*19*).

Preparation of diphenylphosphinomont-

morillonite (**4A**). To chloromontmorillonite (**3**) (5 g) in a 250-ml RB flask, LiP $(C_6H_5)_2$ (4 M excess) synthesised as described in the literature (*20*) was added under nitrogen atmosphere. On addition to *3* the orange-coloured solution of LiP $(C_6H_5)_2$ turned black. The reaction mixture was refluxed for 24 h with constant stirring under nitrogen atmosphere, cooled to room temperature, filtered, and washed consecutively with THF, methanol, methanol + water, acetone, THF, and acetone. The product was vacuum dried and stored.

*Preparation of triphenylphosphinomontmorillonite (***5A***)*. A solution of diphenyl-p-bromophenylphosphine (4 g, 11.8 mmol) (*21*) was taken in a three-necked 100-ml RB flask, containing a nitrogen inlet, a reflux condenser, and a silicone rubber septum. The flask was cooled from −60 to −80°C; *n*-BuLi in hexane (15 ml, 24 mmol) was injected into the flask through the silicone rubber septum in 10 min to give a reddish-brown diphenyl-p-lithiumphenylphosphine product (*22*). The product was stirred for 30 min and was allowed to attain room temperature. Vacuum dried *3* (5.5 g) was added to the reaction flask. The reddish-brown solution turned black immediately. The reaction mixture was refluxed with constant stirring for 8 h, cooled to room temperature, and filtered under nitrogen atmosphere. The residue was washed consecutively with THF, methanol, methanol + water, acetone, and THF and dried under vacuum.

Preparation of 4-picolylmontmorillonite (**6A**). THF (30 ml) was placed in a three-necked 250-ml RB flask equipped with a N_2 inlet, a reflux condenser, and a silicone rubber septum. Liquid commercial 4-picoline (1.2 ml, 12.32 mmol) was injected into the THF via the silicone rubber septum, stirred, and cooled to −20°C. *n*-BuLi in *n*-hexane (15 ml, 24 mmol) was injected dropwise in 10 min to give a yellow-coloured solution of lithiated picoline. With nitrogen allowed to flow, the silicone rubber septum was removed and **3** (5 g) was added to the lithiated solution. The colour of the solution immediately turned black. Later the reaction mixture was stirred for 1 h and allowed to attain room temperature. The reaction mixture was then refluxed for 8 h, cooled to room temperature, and filtered under N_2 atmosphere. The residue was thoroughly washed to give 4-picolylmontmorillonite (**6A**). Ligand **6A** was vacuum dried and stored.

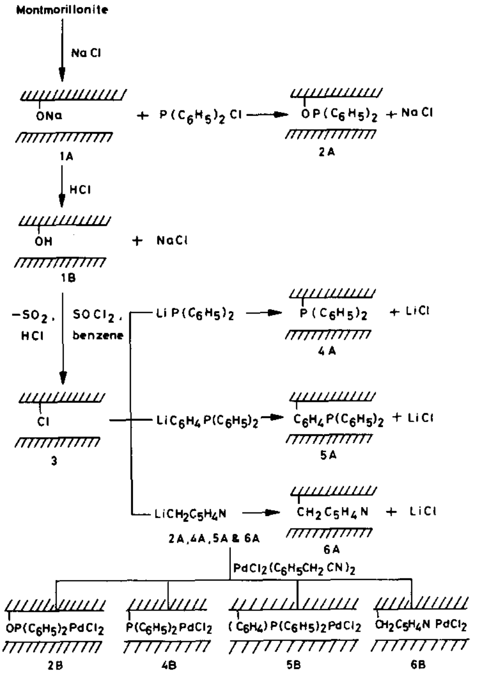
Synthesis of palladim (II)-anchored montmorillonite catalysts (**2B, 4B, 5B,** and **6B**). Functionalised montmorillonite was added to a solution of dichlorobis(benzylcyano)palladium(II) -complex (*23*) in benzene and kept under stirring for 3 h at room temperature until all the golden-yellow colour of the palladium complex disappeared to give palladium(II)-anchored montmorillonite. The product was recovered by filtration and washed with dry benzene until the filtrate become colourless. The residue was dried under vacuum and stored.

2.3. *General Hydrogenation Procedure*

A typical procedure for hydrogenation is as follows. Hydrogenation reactions were carried out in a 100-ml RB flask; the sidearm was fitted with a silicone rubber septum and the other neck was attached through a three-way stopcock to the glass vacuum manifold equipped with a manometer, a gas burette, and a gas -inlet. A flask shaker was used to agitate the reaction mixture. A weighed amount of the catalyst was placed in the flask along with dry solvent. The system was degassed and purged with hydrogen. The catalyst was pretreated for 20 min with hydrogen. A weighed amount of organic reactant (the substrate) was introduced into the preequilibrated hydrogen flask. The uptake of hydrogen was followed every minute.

The products were analyzed on gas chromatograph (Chromatography and Instruments Company, India). The separation was carried out using 10% carbowax 20 *M* TPA on chrom-w 60–80 mesh.

IR spectra of the functionalised montmorillonites and their complexes were recorded as KBr pellets in the region 4000–400



SCHEME 1. Synthesis of organofunctionalised montmorillonites.

cm^{-1} and CsI-disks in the region 400–200 cm^{-1} on a Perkin–Elmer 283B spectrometer. XRD patterns were recorded on a Philips PW 1051 diffractometer as thin films with Ni-filtered CuKα radiation(λ = 1.54138 Å). For measurements a Vacuum Generators ESCALAB 2 instrument was used with MgKα radiation (1253.6 eV) (corrected to Si 2sE_B = 153.4 ± 0.2 eV). Solid-state CP/MAS ^{31}P proton decoupled (10 G) NMR spectra were recorded on a Bruker CXP-300 unit at 121.46 MHz operating at 7.047 T. Spectra were accumulated with 4s recycle time and 10-ms CP contact. Centre band or isotropic chemical shifts were identified in the samples by recording spectra at three different spinner frequencies (4.3 and 2 KHz respectively). They were recorded with reference to external 85% H_3PO_4 acid. The error in determination was estimated to be ± 2.0 ppm.

3. RESULTS AND DISCUSSION

3.1. Characterisation

Montmorillonite is known to participate in Friedel–Crafts reactions, esterification, etherification, and phenylation to form stable covalently bonded organic moieties (*19*).

Montmorillonite is thus functionalised with various phosphines and picolines as described in Scheme 1. Further, they are complexed with palladium. The IR spectra of the functionalised montmorillonites **2A**, **4A**, and **5A** and their palladium catalysts **2B**, **4B**(i, ii, iii), and **5B** exhibit a strong band in the region of 1440 cm^{-1}, due to C=C stretching of the phenyl group attached to phosphorus (*24*, *25*), in addition to characteristic montmorillonite absorption peaks (*26*). Ligand **6A** and its palladium complex **6B** exhibit bands at 1590 and 1615 cm^{-1}, respectively, attributable to complexation of anchored pyridyl nitrogen. The results are consistent with those for polyvinyl pyridylanchored palladium (II) catalysts (*27*). In addition, all catalysts **2B**, **4B**, **5B**, and **6B** exhibit a band at 350 cm^{-1} assigned to the Pd–Cl terminal/trans-bond (*28*).

XRD analyses of all samples were performed in thin films prepared by spreading about 0.5 ml of a dry THF suspension of the sample on a glass slide and drying the slide at room temperature. By using this method the plate-like particles presumably oriented themselves so that the 001 reflection was amplified compared with a powder sample. Thus, the organofunctionalised montmorillonites **2A**, **4A**, **5A**, and **6A** exhibit d_{001} spacing in the region 14.50 to 15.25 Å and these are attributed to the anchored ligands (Table 1). All the functionalised montmorillonites on complexation with palladium give rise to new peaks in the region 15.25 to 18.40 Å due to anchored palladium in montmorillonite interlayer spaces.

In recent years the development of high-power proton decoupling (*29*), crosspolarization (CP) (*30*), and magic angle spinning (MAS) (*31*) techniquess has afforded high-resolution NMR spectra of dilute nuclei of

TABLE 1

Elemental Analyses, XRD, and ESCA Data

No.	Compound	Empirical Pd : P : Cl	Atomic ratio Pd : N : Cl	d_{001} Spacings (Å)	ESCA B.E. Pd $3d_{5/2}$ (eV)	FWHM (eV)
1	**2A**	—	—	15.00	—	—
2	**2B**	1 : 1.6/1.94	—	15.30	338.46	2.2
3	**4A**	—	—	15.40	—	—
4	**4B**(i)	1 : 3.1 : 2.15	—	—	—	—
	4B(ii)	1 : 1.6 : 2.12	—	—	—	—
	4B(iii)	0.99 : 1 : 2.1	—	18.00	338.6	2.7
5	**5A**	—	—	15.30	—	—
6	**5B**	1 : 1.08 : 2.10	—	18.30	338.98	2.4
7	**6A**	—	—	14.20	—	—
8	**6B**	—	1 : 1.2 : 2.1	17.80	339.00	2.8

solid samples. The high abundance of ^{31}P (100%), ($I = \frac{1}{2}$) and generation of metal ^{31}P coupling make these techniques highly sensitive and extremely elucidating for studies of homogeneous transition metal complexes (*32*) and surface-anchored polymer–silica transition metal phosphine complexes (Rh, Pt, Pd, and Ni) (*33–35*) and very recently for characterising phosphinated silica-anchored carbonyl osmium clusters (*32*).

In Fig. 1 sample **2A**, a peak appeared at 7 ppm which on complexation shifted to 30.1 ppm. Here all the anchored phosphorus is complexed with Pd(II). Similarly for **5A** on complexation with Pd(II) (**5B**), a downfield shift to 29.4 ppm is observed with simultaneous disapperance of a peak at 7.2 ppm assigned to ligand phosphine.

CP MAS spectra of **4A** exhibit a threefold anisotropic centre band with a maximum at 16.1 ppm having a linewidth of half maximum height $\Delta v_{1/2}$ of 150 Hz and assigned to P(III) nuclei and not due to pentavalent phosphine oxide, as is evident from the high isotropic chemical shift value of phoshine oxide, $Ph_3P{=}O$, 29.2 ppm (*34*). Sample **4A** is complexed with difference proportions of palladium approximating to Pd/P ratios of 1/3, **4B**(i); 1/1.5, **4B**(ii); and 1/1, **4B**(iii) to understand the nature of complexation. CP MAS spectra of **4B**(i, ii, and iii) with different ratios of Pd/P show a central band with three different finely resolved isotropic chemical shifts, ΔS, of varying intensities in the regions 10.5, 16.9, and 23.7 ppm, respectively, and a total line width of 200 Hz. The deshielded peak at 23.7 ppm is attributed to phosphorus complexed with Pd(II) as observed in various phosphine–Pd(II) complexes, whereas peaks at 10.5 and 16.9 ppm are due to unreacted finely resolved anchored phosphorus.

Further evidence came from the examination of the spectra of samples **4B** (itoiii), where the peak at 23.7 ppm assigned to the complexed phosphorus with Pd(II) is progressively intensified on increased Pd/P ratio and finally spectrum **4B**(iii) shows a total disappearance of the peaks at 10.5 and 16.9 ppm. These results are best correlated with the elemental analyses, too. Thus, indication for the formation of monophosphine–Pd complexes, even in the low ratios of Pd/P, is available with these results, unlike in polymeranchored complexes, where it is possible to complex more than one phosphorus anchored at different sites due to backbone flexibility (*1*). These results suggest a rigidity of montmorillonite interlayer channels disallowing complexation with a second phosphine group anchored at different sites.

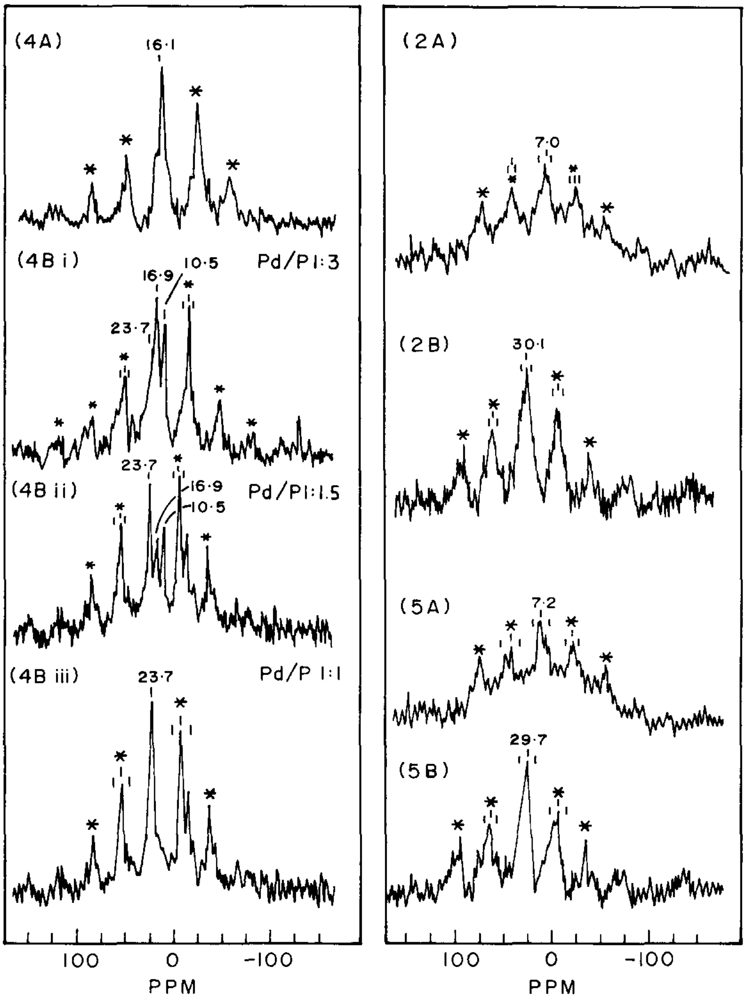


FIG. 1. Solid-state ^{31}P NMR spectra with magic angle spinning.

The deshielding of the phosphorus nucleus on complexation with Pd(II), chemical shift, and $\Delta v^{1/2}$ values substantially demonstrates that phosphorus in **2A** and **4A** exists in the trivalent state and not in the undesirable saturated pentavalent state or as phosphonium ion.

The line broadening of the substantial shift dispersion to the extent of 150–200 Hz in the samples is because of the disordered environment of ^{31}P nuclei in the lattice of montmorillonite, as observed earlier for CP MAS spectra of *cis*-$PtCl_2$ $[PPh_2 \cdot CH_2CH_2Si(oEt)_3]_2$, which exhibits a centre component in the shift range of 10 ppm (15.3, 12.9, 4.8 ppm, respectively) and with a line width of 500 Hz (*34*). The presence of an anisotropic centre band with three different isotropic chemical shifts is echoed in the side bands as evident in Fig.1 and is due to the presence of three different phosphorus environments in the restricted lattice of montmorillonite.

The ESCA results of all montmorillonite-anchored palladium catalysts **2B**, **4B**, **5B**, and **6B** exhibit well-resolved doublets with binding energies of Pd $3d^{5/2}$ in the region 338 to 339 eV and with full width at half maximum (FWHM) spread over 2.0 to 3.0 eV as shown in Fig. 2. Thus three results indicate that palladium is present in the divalent state.

The phosphorus binding energies in the phosphinated montmorillonites **2A**, **4A**, and **5A** and in the palladium(II) catalysts **3B**, **4B**, and **5B** remain more or less in the region 132 eV; i.e., the electron density around the phosphorus is practically the same both before and after coordination. Coordination by simple electron pair sharing is expected to give a decrease in the electron density of the ligand. In view of this, the binding energies of the core electrons of the actual donor atoms of the ligand exhibit larger values. This effect will be altered where π-bonding involves back-donation from filled metal orbitals to empty ligand orbitals. Thus the effect of π-bonding is expected to counteract the effect of σ-bonding causing insignificant change in the electron density on the actual donor atoms of the ligand. Hence, the binding energies of these atoms do not alter on complexation. Parallel to this observation, the phosphorus binding energies in free triphenylphosphine, $P(C_6H_5)_3$, the π-acceptor ligand, is 131.9 eV and in its metal complex, $(PdCl_2(P(C_6H_5)_3)_2$, is 131.7 eV (*37*); i.e., it remains the same or decreases slightly to the extent of 0.1 to 0.2 eV.

The electron density around 4-picolylmontmorillontie and anchored palladium (II) picolylmontmorillonite is the same as in homogeneous and polymer-anchored palladium analogues in the region 499.0 to 500.0 eV and this is also due to the synergic effect (*27*).

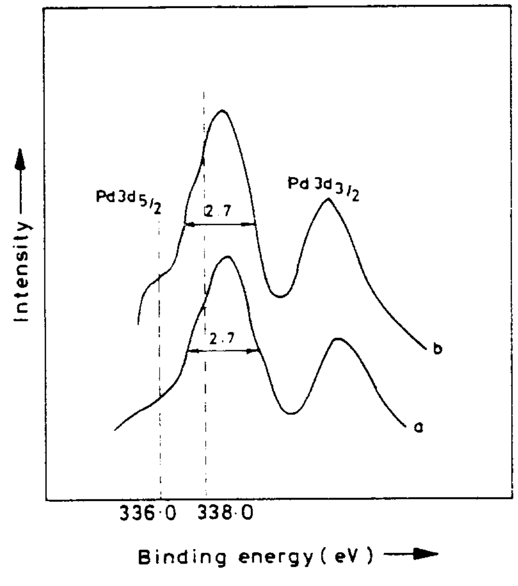


FIG. 2. ESCA spectra of Pd 3*d* level for catalyst **4B**(ii): (a) Fresh catalyst; (b) used catalyst.

All the catalysts except **4B**(i) and **4B**(ii) exhibit an atomic ratio of approximately 1 : 1 : 2 of palladium, phosphorus/nitrogen, and chlorine, respectively, corresponding to $PdCl_2$ anchored to support via pendant ligands in its elemental analysis (Table 1). Thus palladium is present in the +2 oxidation state and in the coordinatively unsaturated (tricoordinate) state. ESCA further conclusively proves the divalency of palladium in the catalyst. However, the technique is not ideal enough to determine the oxidation state of phosphorus due to the close binding energy values of trivalent and pentavalent phosphorus. Solid-state ^{31}P NMR is a suitable technique for determining the electronic environment around phosphorus nuclei and has unambiguously substantiated the existence of trivalent phosphorus and absence of pentavalent phosphorus and phosphonium ion in the ligand and complexation of phosphorus in the complex. The existence of intense rotational side bands indicates the presence of the anchored moiety in the interlayer spaces. The presence of ligands and complexes in the interlayer spaces is substantiated by the XRD spacing. Thus the structures of the catalyst are as shown in Scheme 1.

3.2. Hydrogenation Activity

All the catalysts **2B–6B** were evaluated in hydrogenation reactions of styrene and hex-1-ene and compared with Pd/C and polymer-anchored catalysts. The rates decreased in the order **4B**(ii) > **4B**(iii) > **4B**(i) > Pd/C > **2B** > **6B** > Polymer-anchored > **5B** (Table 2). Rates measured were initial reaction rates, which were the maximum rates observed. These results indicate that catalyst **4B** is more highly active than the other montmorillonite-functionalised catalysts and also than Pd/C and polymer-anchored catalysts. The Brønsted acidity in the

TABLE 2

Hydrogenation of Styrene and Hex-1-ene by Various Heterogenised Palladium(II) Catalysts[a]

Catalyst	Cycle No.	Rate[b]	
		Styrene	Hex-1-ene
2B	1	8	3
5B	1	5	3
6B	1	6	3
Polymer-anchored Phosphine complex	1	6	4
Pd/C	1	15	14
4B(i)	1	15	10
4B(iii)	1	23	16.5
4B(ii)	1	24	17
	2	23.8	16.8
	3	23.9	16.8
	4	24.1	17.0
	5	24.0	17.2
	6	24.2	16.8
	7	24.4	17.2
	8	23.8	17.0
	9	24.2	17.1
	10	24.0	17.2
	20	24.2	16.9

[a] Hydrogenation reactions were carried out at room temperature and atmospheric pressure of hydrogen with 2.0 mmol of organic reactant and 0.020 mmol of **4B** in THF solvent.

[b] Milliliters of hydrogen absorption per minute. Conversion was quantitative in every cycle. Products were analyzed by GLC periodically.

montmorillonite support stems from the bridging basal oxygens. Thus, the support can be regarded as a solid acid which helps in the polarisation of alkene or alkyne molecules in the interlayer spaces, forming the carbocations and facilitating the hydride transfer from the metal complex (*38, 39*). Therefore, the high activity in the montmorillonite interlayer spaces for the complex **4B** can be assumed to be due to the change in electronic environment imposed by the acidic support. Further, the high reactivity of **4B** can be speculated as being due to the tricoordinated palladium complex as evidenced from ^{31}P NMR data.

3.3. Selectivity

Since **4B**(ii) with medium palladium loading (3.6%) is found to be superior to **4B**(i) (1.8%) and **4B**(iii) (5.65%), it was decided to use the **4B**(ii) catalyst for further studies in the hydrogenation of various alkynes and alkenes. Table 3 (see also Fig. 3) shows the high activity of **4B**(ii) in sequential selective hydrogenation of alkynes to alkenes and to alkanes. Yields are almost quantitative. Although the rate of hydrogenation of alkenes to alkanes is higher than that of alkyne to alkene, the sequential selectivity is highly impressive and can be attributed to the higher nucleophilicity of the alkynes that enables preferential binding to the palladium complex in catalytic hydrogenation.

The internal triple/double bonds are also hydrogenated but with a decreased rate of hydrogen absorption. The hydrogenation reactions are versatile as is evident from the hydrogenation of varied alkynes and alkene differing in the steric and electronic environment around the C=C bond. In contrast, the hydrogenation of propargyl alcohol and acetylene dicarboxylic acid dimethyl ester has taken a longer time with analogous polymer-anchored palladium complexes (*40*).

The selective hydrogenation of hexyne to hex-l-ene without any isomerization is very impressive. Thus the selective semihydro-

TABLE 3

Hydrogenation Rate of Various Alkynes to Alkanes via Alkene Stage[a]

Alkyne reactant	Hydrogenation rate[b,c]	
	Ene	Ane
Phenylacetylene	14	234
Diphenylacetylene	14	18
Dimethylacetylene dicarboxylate	18	22
Phenylpropyne	15	18
Butynediol	10	12
1-Hexyne	14	17
Propargyl alcohol	10	17

[a] Sequential hydrogenation reactions were carried out at room temperature and atmospheric pressure of hydrogen in tetrahydrofuran with 2.0 mmol of alkyne and 0.02 mmol of **4B** as catalyst.

[b] Milliliters of H_2 uptake per minute. Conversions were quantitative at each stage and selectivity to alkenes from alkynes was always >98% at 100% conversion.

[c] Products were analyzed by GLC periodically.

genation of alkynes to alkenes is almost comparable with the best catalyst such as Lindlar and Osborn's cationic complex *(41)*. For example, the striking failure of Lindlar's catalyst is observed in the semihydrogenation of ethylphenyl propiolate, which gave totally hydrogenated product. Similarly a rhodium cationic complex afforded poor selectivity in the semihydrogenation of 1,4-butynediol, although the selectivity exhibited by the complex is as high as 99% in most of the cases.

3.4. Size Selectivity

Size selectivity of organic reactant substrates can be induced by controlling the interlayer spacing of montmorillonite by incorporating different complexes. Thus catalysts with different initial interlayer spacings which will swell further depending on the dielectric constant of solvents used *(42)* are employed to examine the rate of reactivity of the substrates with different critical dimensions in hydrogenation reactions. Catalyst **4B**(ii) hydrogenated mono-and disubstituted alkynes and alkenes in ethanol (Table 4).

TABLE 4

Hydrogenation of Various Organic Substrates with Catalysts **2B** and **4B**[a]

No.	Organic substrate	Rate, ml of hydrogen uptake min^{-1} (mmol Pd)$^{-1}$		Critical dimension[b] (Å)
		2B Ethanol	**4B**(ii) Ethanol	
1	Phenylacetylene	150	500	9.6
2	Styrene	515	1000	9
3	Diphenylacetylene	1	500	13.84
4	Stilbene	1	750	13.28

[a] Hydrogenations were carried out at room temperature and atmospheric pressure of hydrogen with 2.0 mmol of substrate and 0.02 mmol of **2B** or **4B**, in each case.

[b] Calculated from Dreiding models.

On the other hand catalyst **2B** selectively hydrogenated monosubstitued alkynes and alkenes under similar conditions. No hydrogen absorption was recorded for diphenylacetylene and trans-stilbene. The ratios of the rates of hydrogenation of styrene to phenylacetylene for catalysts **2B** and **4B** are 3.3 : 1 and 2 : 1, respectively. In catalyst **2B** with its lower initial interlamellar spacing there is an induced size selectivity as evidenced in the higher rates of hydrogenation (styrene/phenylacetylene) and selective hydrogenation of monosubstituted substrates only. Conversely, catalyst **4B** with its higher interlamellar spacing has not shown any size selectivity. The origin of size selectivity can be correlated to the orientation and spatial requirement of the substrate–palladium complex in the interlamellar spaces of montmorillonite. The size selectivity displayed by catalyst **2B** can be thought of as arising from the fact that the complexed substrate preferred orientation is perpendicular or nearly perpendicular to the interlayer spaces of montmorillonite, as proposed by Pinnavaia *et al.* *(6)*. In these orientations the disubstituted substrates (13.13 Å) require higher spacing than the monosubstituted substrates (9–9.5Å).

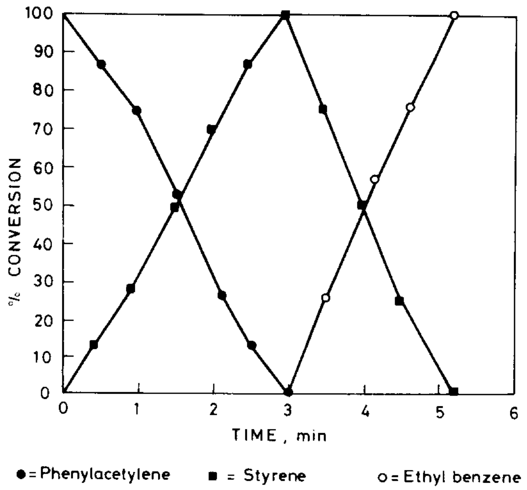


FIG. 3. Sequential hydrogenation of phenylacetylene to ethylbenzene via styrene.

3.5. Recycling Capacity

Catalyst **4B**(ii) has shown consistent activity in the hydrogenation of styrene and hex-l-ene for 20 recycles, as described in Table 2. The retention of activity over several recycles indicates that there is no significant loss of active metal in recycling this catalyst. This is confirmed by the absence of palladium in the filtrate. Furthermore, the used catalyst was tested in the hydrogenation of various substrates (Table 5). The rate of hydrogen absorption is almost the same as that of the fresh catalyst under identical conditions. The consistent activity is ascribed to the presence of interlayer basal oxygens that act as polydentate centres to hold the decoordinated metal from the phosphines within the interlayer region without diffusing out and facilitating recoordination with phosphines. Excess uncomplexed phosphines present in interlayer channels must also have helped this process. Hence the activity and consistency for number of recycles with sample **4B**(ii) having a Pd/P ratio of 1/1.5, are superior to those of sample **4B**(iii) which has a Pd/P ratio of 1/1. It is well known that the active metal species in homogeneous catalytic reactions is not always what is expected. It is also possible that the reaction may involve colloidal particles. However, the evidence obtained from ESCA data of the used catalyst indicated that palladium is present in the divalent state (Fig. 2) and a minor and negligible amount of palladium metal formation is observed. This is supported by the MAS CP NMR spectra of used catalyst, which shows an almost identical pattern when compared with fresh catalyst.

TABLE 5

Hydrogenation of Various Organic Substrates with Used Montmorillonite-Bound Palladium(II) Catalyst **4B**[a]

Organic substrate	Rate[b]
Phenylacetylene	13.8
Styrene	24.2
Stilbene	17.8
Hex-1-ene	17.1

[a] Hydrogenation reactions were carried out at room temperature and atmospheric pressure of hydrogen with 2 mmol of substrate and recovered **4B**(ii) in THF solvent.

[b] Milliliters of hydrogen absorption per minute. Conversions were quantitative. Products were analysed by GLC periodically.

CONCLUSIONS

Various functional groups (diphenylphosphine, triphenylphosphine, and 4-picoline) have been covalently intercalated in montmorillonite. Complexation with Pd has led to the synthesis of various interlamellar ligated montmorillonite Pd complexes. Elemental analysis, IR, XRD, NMR, and ESCA results demonstrate that palladium complexed with phosphorus/nitrogen is in the divalent and tricoordinate state. Diphenylphosphine–palladium complex **4B**(ii) (Pd/P 1/1.5), a coordinately unsaturated complex has shown consistent activity for a number of recycles in the hydrogenation of styrene and hex-l-ene. The consistent activity is ascribed to the presence of interlayer basal oxygens that act as polydentate centres to hold the decoordinated metal from the phosphines within the interlayer region without diffusing out, and thereby facilitating recoordination with phosphines. Excess uncomplexed phosphines present in the interlayer channels also compete for complexation with palladium during this process and thus prevent the metal leaching. With the recycling capacity, the use of these catalysts can become a potential alternative to other catalysts. The preferential selectivity towards alkynes can be attributed to the higher nucleophilicity of the alkynes that enables the preferential binding to the palladium complex.

The complex with an initial lower interlayer spacing hydrogenated terminal alkynes and alkenes only, while the complex with a higher interlayer spacing hydrogenated both internal and terminal unsaturation. With the easy adjustment of the interlayer spacings by the incorporation of complex moieties of varying size, montmorillonite offers a practical alternative to zeolites which have a fixed dimension for inducing size selectivity.

REFERENCES

1. Pittman, Jr., C. U., *in* "Comprehensive Organometallic Chemistry" (G. Wilkinson, Ed.), Vol. 8, p. 553. Pergamon, New York, 1982.

2. Yermakov, Yu. I., Kuznetsov, B. N., and Zakharov, V. A., "Studies in Surface Science and Catalysis." Elsevier, Amsterdam, 1981.
3. Jones, R.A ., and Seeberger, M. H., *J. Chem. Soc. Chem. Commun.*, 373 (1985).
4. Nayak, S. D., Mahadevan, V., and Srinivasan, M., *J. Catal.* **92,** 327 (1985).
5. Bergbrieter, D. E., and Chandran, R., *J. Am. Chem. Soc.* **109,** 174 (1987).
6. Pinnavaia, T. J., Raythatha, R., Lee, J. G. S., Halloran, L. J., and Hoffman, J. F., *J. Am. Chem. Soc.*, **101,** 6891 (1979).
7. Shimazu, S., Hirano, T., and Uematsu, T., *Appl. Catal.* **34,** 255 (1987).
8. Shimazu, S., Tuamoto, W., Iba, T., Miura, M., and Uematsu, T., *Catal. Today* **6,** 141 (1989).
9. Choudary, B. M., Ravi Kumar, K., Zafar Jamil, and Thyagarajan, G., *J. Chem. Soc. Chem. Commun.*, 931 (1985).
10. Ravi Kumar, K., Choudary, B. M., Zafar Jamil, and Thyagarajan, G., *J. Chem. Soc. Chem. Commun.*, 130 (1986).
11. Choudary, B. M., and Bharathi, P., *J. Chem. Soc. Chem. Commun.*, 1505 (1987).
12. Choudary, B. M., and Ravi Kumar, K., *Appl. Catal.*, **35,** 177 (1987).
13. Shimazu, S., Ishida, T., Uematsu, T., *in* "Proceedings, 9 International Congress on Catalysis, Calgary, 1988" (M. J. Philips and M. Terman, Eds.), Vol. 4, p. 1913. Chem. Institute of Canada, Ottawa, 1988.
14. Shimazu, S., Ishida, T., and Uematsu, T., *J. Mol. Catal.* **55,** 353 (1989).
15. Herzog, S., Dehnert, J., and Luhder, K., *in* "Techniques of Inorganic Chemistry" (H. B. Jonassen and A. Weissberger, Eds.), Vol. 8, p. 123. Interscience, New York, 1968.
16. Posner, A. M., and Quirk, J. P., *Proc. R. Soc. London Ser. A.*, **278,** 35 (1964).
17. Spencer, W. F., and Gieseking, J. E., *J. Phys. Chem.* **56,** 751 (1951).
18. Ballatine, J. A., Jones, W., Purnell, J. H., Tennakoon, D. T. B., and Thomas, J. M., *Chem. Lett.*, 763 (1985).
19. Gentili, R., and Deuel, H., *Helv. Chim. Acta.* **40,** 106 (1957).
20. Lieto, J., Milstein, D., Albright, R. L., Minikiewicz, J. V., and Gates, B. C., *Chem. Tech.* **13,** 46 (1983).
21. Baumgarten, H. E., "Organic Synthesis," Vol. 5, p. 496. Wiley, New York, 1973.
22. Baldwin, R. A., Cheng, M. T., *J. Org. Chem.* **32,** 1572 (1967).
23. Choudary, B. M., *Indian J. Chem. Sect. A* **26,** 61 (1987).
24. Bellamy, L. S., "The Infrared Spectroscopy of Complex Molecules," Vol. 1, p. 348, Chapman & Hall, London, 1980.
25. Pouchert, C. J., "The Aldrich Library of Infrared Spectra," p. 1181, Aldrich Chemical Co. Inc., Wisconsin, 1981.
26. Van Der Marel, H. W. and Beutelspacher, H., "Atlas of Infrared Spectroscopy of Clay Minerals and their Admixtures," Vol. 57. Elsevier, Amsterdam/New York, 1976.
27. Karklin L. N., Klyuev, M. V., and Pomogailo, A. B., *Kinet Catal* **24,** 343 (1983).
28. Adams, D., *in* "Metal Ligand and Related Vibrations: A Critical Survey of Infrared and Raman Spectra of Metallic and Organometallic Compounds" 1st Edn., Arnold, London, 1967, p. 74.
29. Schaefer, J., and Stejskal, E. O., *J. Am. Chem. Soc.* **98,** 1031 (1976).
30. Pines, A., Gibby, M. G., and Waugh, S. S., *J. Chem. Phys.*, **56,** 1776 (1972); **59,** 569 (1973).
31. Andrew, E. R., *Prog. Nucl. Magn. Reson. Spectrosc.* **8,** 1 (1971).
32. Pregosin P. S., and Kunz, R. W., "Basic Principles and Progress in NMR," Vol. 16. Springer, Berlin, 1979; Diesveld, J. W., Menger, E. M., Edzes, H. T., and Veeman, W. S., *J. Am. Chem. Soc.* **102,** 7935 (1980).
33. Naaktgeboren, A. J., Nolte, R. J. M., and Drenth, W., *J. Am. Chem. Soc.* **102,** 3350 (1980).
34. Bemi, L., Clark, H. C., Davies, J. A., Fyfe, C. A., and Wasylishen, R. E., *J. Amer. Chem. Soc.* **104,** 438 (1982).
35. Fyfe, C. A., Clark, H. C. Davies, J. A., Hayes, P. J. and Wasylishen, R. E., *J. Am. Chem. Soc.* **105,** 6577 (1983).
36. Alexiev, R. V. D., Clayden, N. J., Cook, S. L., Dobson, C. M., Evans, J., and Smith, D. J., *J. Chem. Soc. Chem. Commun.*, 938 (1986).
37. Blackburn, J. R., Nordberg, R., Stevie, F., Albridge, R. G., and Jones, M. M., *Inorg. Chem.* **9,** 2374 (1970).
38. Lazlo, P., *Acc. Chem. Res.* **19,** 121 (1986).
39. Occelli, M. L., Hsu, J. T., and Galya, L. G., *J. Mol. Catal.* **33,** 371 (1985).
40. Kaneda, K., Terasawa, M., Imanaka, T., and Teranishi, S., *in* "Fundamental Research in Homogeneous Catalysis" (M. Tsutsui, Ed.), Vol. 3, p. 671 Plenum, New York, 1979.
41. Schrock, R. R., and Osborn, J. A., *J. Am. Chem. Soc.* **98,** 2143 (1976).
42. Murray, R. S., and Quirk, J. P., *Soil Sci. Soc. Am. J.* **46,** 865 (1982).