22 April 1983, Volume 220, Number 4595 **SCIENCE**

Intercalated Clay Catalysts

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Summary. Recent advances in the intercalation of metal complex cations in smectite clay minerals are leading to the development of new classes of selective heterogeneous catalysts. The selectivity of both metal-catalyzed and proton-catalyzed chemical conversions in clay intercalates can often be regulated by controlling surface chemical equilibria, interlamellar swelling, or reactant pair proximity in the interlayer regions. Also, the intercalation of polynuclear hydroxy metal cations and metal cluster cations in smectites affords new pillared clay catalysts with pore sizes that can be made larger than those of conventional zeolite catalysts.

The swelling phyllosilicate minerals known as smectite clays constitute a naturally occurring class of inorganic catalysts. These ubiquitous minerals are components of many soils and sediments and often are found as large, mineralogically pure deposits (1). Because of their small particle size (< 2 micrometers) and unusual intercalation properties, they afford an appreciable surface area for the adsorption of organic molecules and catalysis. Indeed, the probable catalytic role of smectites has been recognized in several "natural" processes (2), including petroleum-forming reactions (3, 4), chemical transformations in soils (5–7), and reactions related to chemical evolution (8–13).

More than 50 years ago, Eugene Houdry found that acid-modified smectites provided gasoline in high yield when used as petroleum-cracking catalysts (14). These modified clays were used extensively as commercial catalysts until the mid-1960's, when they were replaced by more thermally stable and selective zeolite catalysts. Smectite clays are still used today as commercial catalysts, but only in minor quantities. Oleic acid dimerization, for example, is accomplished best with a smectite clay catalyst (15).

Recent advances in the intercalation chemistry of smectite clays has rekindled interest in these minerals as catalysts or catalyst supports. One new class of intercalates incorporates metal complex catalysts between the silicate layers. Although the immobilization of complex catalysts in clay structures makes it possible to conduct solution-like reactions in the solid state and to minimize many of the technical and economic barriers associated with the use of homogeneous solution catalysts, the advantages of catalyst intercalation go beyond mere immobilization. By mediating the chemical and physical forces acting on interlayer reactants, one often can improve catalytic specificity relative to homogeneous solution.

A second new class of smectite intercalation compounds makes use of robust cations as molecular props or pillars between the silicate layers. The pillaring phenomenon leads to the formation of porous networks analogous to zeolites. Since pillared clays can have pore sizes larger than those of zeolites, they offer a promising new means of facilitating the reactions of large molecules.

Smectite Structures

Smectite clay minerals have layer lattice structures in which two-dimensional oxyanions are separated by layers of hydrated cations. Figure 1 schematically illustrates the oxygen framework of a layer. The oxygen atoms define upper and lower sheets of tetrahedral sites and a central sheet of octahedral sites. The 2:1 relation between the tetrahedral and octahedral sheets within a layer allows the smectite clays to be classified as 2:1 phyllosilicates. This structural designation differentiates smectites from 1:1 clay minerals, such as kaolinite, in which the layers are formed by coupling of only one tetrahedral sheet to an octahedral sheet (16).

The members of the smectite group of clays are distinguished by the type and location of cations in the oxygen framework. In a unit cell formed from 20 oxygens and four hydroxyl groups there are eight tetrahedral sites and six octahedral sites. When two-thirds of the octahedral sites are occupied by cations, the mineral is classified as a dioctahedral 2:1 phyllosilicate. A trioctahedral 2:1 phyllosilicate has all octahedral sites filled by cations.

Idealized structural formulas are presented in Table 1 for three dioctahedral smectites and two trioctahedral smectites. Included for comparison are structural formulas for two micas (muscovite and phlogopite) and pyrophyllite and talc. These latter minerals, though not smectites, have the same 2:1 phyllosilicate oxygen framework found in smectites.

In talc all of the tetrahedral and octahedral sites in the oxygen framework are filled by Si^{4+} and Mg^{2+}, respectively, and the layers are electrically neutral. In pyrophyllite, electrical neutrality of the layers is achieved by the presence of Si^{4+} in all eight tetrahedral holes and of Al^{3+} in two-thirds of the octahedral holes. Thus, in crystals of talc and pyrophyllite the layers are coupled through relatively weak dipolar and van der Waals forces (17). In contrast to talc and pyrophyllite, the layers in muscovite and phlogopite bear a net charge of $2e$ per

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Table 1. Idealized structural formulas for some dioctahedral and trioctahedral 2:1 phyllosilicates. Trace elements in the formulas have been disregarded for simplicity. In each formula the cations enclosed in brackets occupy octahedral sites and the cations in parentheses occupy tetrahedral sites.

Mineral group	Dioctahedral	Trioctahedral
Pyrophyllite-talc	Pyrophyllite: $[Al_{4.0}](Si_{8.0})O_{20}(OH)_4$	Talc: $[Mg_{6.0}](Si_{8.0})O_{20}(OH)_4$
Smectites	Montmorillonite: $M^{n+}_{x/n} \cdot yH_2O[Al_{4.0-x}Mg_x](Si_{8.0})O_{20}(OH)_4$	Hectorite: $M^{n+}_{x/n} \cdot yH_2O[Mg_{6.0-x}Li_x](Si_{8.0})O_{20}(OH,F)_4$*
	Beidellite: $M^{n+}_{x/n} \cdot yH_2O[Al_{4.0}](Si_{8.0-x}Al_x)O_{20}(OH)_4$	Saponite: $M^{n+}_{x/n} \cdot yH_2O[Mg_{6.0}](Si_{8.0-x}Al_x)O_{20}(OH)_4$
	Nontronite: $M^{n+}_{x/n} \cdot yH_2O[Fe_{4.0}](Si_{8.0-x}Al_x)O_{20}(OH)_4$	
Micas	Muscovite: $K_2[Al_{4.0}](Si_{6.0}Al_{2.0})O_{20}(OH)_4$	Phlogopite: $K_2[Mg_{6.0}](Si_{6.0}Al_{2.0})O_{20}(OH)_4$

*In this mineral some framework hydroxyls are replaced by fluoride ion.

Si_8O_{20} unit due to a positive charge deficiency which results from the substitution of Si^{4+} by Al^{3+} in tetrahedral positions. The charge deficiency is balanced by interlayer potassium ions, which are coordinated to the hexagonal arrays of oxygen atoms at the layer surface (*18*).

The charge on the layers of smectites is intermediate between the end member mica and the pyrophyllite-talc groups of phyllosilicates. The difference in layer charge results in physical and chemical properties not found for the end members. Typically, the positive charge deficiency in the layers of smectites ranges from 0.4 to 1.2*e* per Si_8O_{20} (*19*). To balance the layer charge, layers of hydrated cations are intercalated between the silicate layers. Normally, the intercalated cations are alkaline earth ions (Ca^{2+}) and sometimes alkali metals (Na^+). In montmorillonite, the most familiar (*20*) and common member of the smectite groups, the layer charge originates from the substitution of octahedral Al^{3+} by Mg^{2+}. Hectorite also is "octahedrally charged" with Li^+ substituting for Mg^{2+} in the octahedral sheet. Beidellite and saponite are tetrahedrally charged smectites with Al^{3+} replacing Si^{4+}. Nontronite can be regarded as a ferruginous analog of beidellite.

The layer charge in octahedrally charged smectites is distributed over all oxygens in the framework. These smectites tend to be turbostratic; that is, the layers are randomly stacked with respect to the in-plane *a* and *b* axes of adjoining layers. The negative charge on the layers of tetrahedrally charged smectites is more localized, and these derivatives tend to exhibit greater three-dimensional order (*21, 22*).

Cation Exchange, Intercalation, and Swelling

Smectite clays possess a combination of cation exchange, intercalation, and swelling properties which makes them unique. Their capacity as cation exchangers is fundamental to their intercalation and swelling properties. This distinguishes smectites from the mica and pyrophyllite-talc groups of minerals, which have little or no ion exchange capacity (*23*). Because of the ability of the minerals to imbibe a variety of cations and neutral molecules, an almost limitless number of intercalates are possible.

The hydrated cations on the interlamellar surfaces of the native minerals can be replaced with almost any desired cation by utilizing simple ion exchange methods. Homoionic exchange derivatives are readily achievable with simple hydrated cations, including hydrated transition metal ions. With large, complex exchange cations, the extent of ion replacement may be size-limited. In hectorite, which typically exhibits a layer charge of 0.67*e* per Si_8O_{20}, the cation exchange capacity on an anhydrous basis is 87 milliequivalents per 100 grams, about one-fifth the exchange capacity of sulfonated styrene-divinylbenzene resins. Since the average distance between exchange equivalents in the mineral is ~ 8.3 Å, cations with cross-sectional diameters greater than this value can fully cover the interlamellar surfaces before 100 percent exchange is reached. Thus, although the interlamellar surface is very large (~ 750 square meters per gram), the size of the exchanging ion can be a limiting factor in determining ion loading.

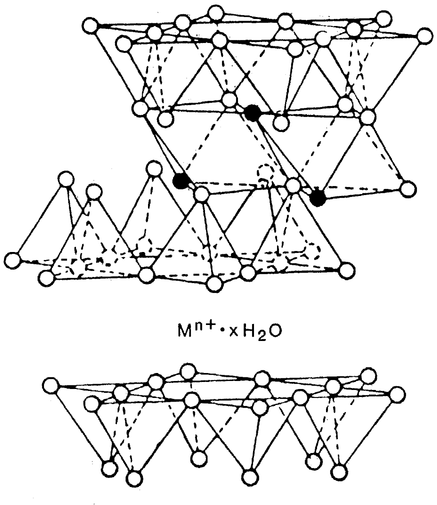


Fig. 1. Idealized structure of a smectite clay mineral. (○) Oxygen atoms; (●) hydroxyl groups. Silicon and sometimes aluminum normally occupy tetrahedral positions in the oxygen framework. Aluminum, magnesium, iron, or lithium may occupy octahedral sites. $M^{n+} \cdot xH_2O$ represents the interlayer exchange cation.

Neutral molecules other than water also can be intercalated between the silicate layers of smectites. Several binding mechanisms may operate in the intercalation processes (*5, 24, 25*). One particularly important mechanism involves complex formation between the exchange cation and the intercalant. Such a mechanism operates in the binding of pyridine (py) to Cu^{2+} exchange forms of smectites (*26*):

$$\overline{\underline{[Cu(H_2O)_x]^{2+}}} + py \xrightarrow{-H_2O} \overline{\underline{[Cu(py)_4]^{2+}}} \quad (1)$$

where the horizontal lines symbolize the silicate layers.

The reaction of the hydrated cation functioning as a Bronsted acid and the intercalant acting as a base is another important intercalation mechanism. Ammonia, for example, binds as ammonium ion in Mg^{2+}-montmorillonite (*27*):

$$\overline{\underline{[Mg(H_2O)_x]^{2+}}} + NH_3 \rightarrow$$

$$\overline{\underline{[Mg(OH)(H_2O)_{x-1}]^+ + NH_4^+}} \quad (2)$$

A variety of experiments have shown that hydrated cations are more acidic in clay interlayers than in homogeneous aqueous solution (*27–31*). The enhanced Bronsted acidity under intercalated conditions is due in part to the polarizing influence of the cation on the water molecule in the spatially restricted interlayers. The interlayer acidity is found to increase with increasing charge-to-radius ratio of the cation and with decreasing water content of the interlayers (*24, 27*).

The most important property of smectites from the standpoint of catalyst design is their ability to expand beyond a single molecular layer of intercalant. The extent of interlayer swelling depends on the nature of the swelling agent, the exchange cation, the layer charge, and the location of the layer charge. The Li$^+$ and Na$^+$ exchange forms of the minerals are particularly susceptible to swelling by water (*22, 32, 33*). As the interlayer water content of Na$^+$-smectites is increased with increasing partial pressure, a more or less constant interlayer spacing corresponding to monolayer formation is observed. After this, the spacing jumps abruptly to a value corresponding to two intercalated water layers. The stepping of the interlayer spacing is especially well behaved in beidellite and saponite (*32*). Further swelling of the interlayers due to osmotic forces is observed when the minerals are immersed in liquid water.

The osmotic swelling of smectite clays can be quite spectacular. Under appropriate conditions the silicate layers can be separated by hundreds of angstroms of water. In fact, the silicate layers of Na$^+$-montmorillonite in dilute aqueous suspension are completely dispersed (delaminated). As the concentration of the dispersion is increased, gelation occurs. The gelation phenomenon, which occurs at a concentration as low as 2 percent clay by weight, is believed to result from layer edge-to-face interactions which generate a "house-of-cards" structure (*34*).

Interlayer Dynamics

Molecular catalysts intercalated in smectite clays are accessible for reaction under ambient conditions, provided the interlayers are swollen to permit rapid diffusion of reagents. Although a solution-like environment exists when the interlayers are highly expanded by a large number of molecular layers of solvent, the physical properties of such phases make them impractical as heterogeneous catalysts. Swollen clay dispersions at low concentrations (< 2 percent by weight) tend to be colloidal and difficult to separate from reaction products. As the concentration is increased, the dispersions thicken and eventually become gel-like masses with high impedance to fluid flow. Therefore, for a clay intercalated molecular catalyst to be useful, the interlayer molecules must be mobile under intermediate degrees of swelling where the intercalate retains the mechanical properties of a genuine solid.

Complementary electron spin resonance (ESR) and nuclear magnetic resonance (NMR) experiments (*35–38*), along with quasi-elastic neutron scattering studies (*39*), have provided incisive information on the interlayer dynamics of clay intercalates. A general picture of the interlayer environment has emerged from these studies. At low degrees of interlayer solvation (for instance, one to three water layers), the solvated exchange cations adopt oriented positions on the interlamellar surfaces. Although oriented, the solvated cations are in a dynamic state and undergo anisotropic rotations about specific molecular axes. Uncoordinated water molecules between the solvated cations are capable of translational diffusion within and between the "cages" defined by the solvated cations and the silicate layers (*39*). Restricted motions and preferred orientations also have been observed for intercalated organic species (*37, 38*).

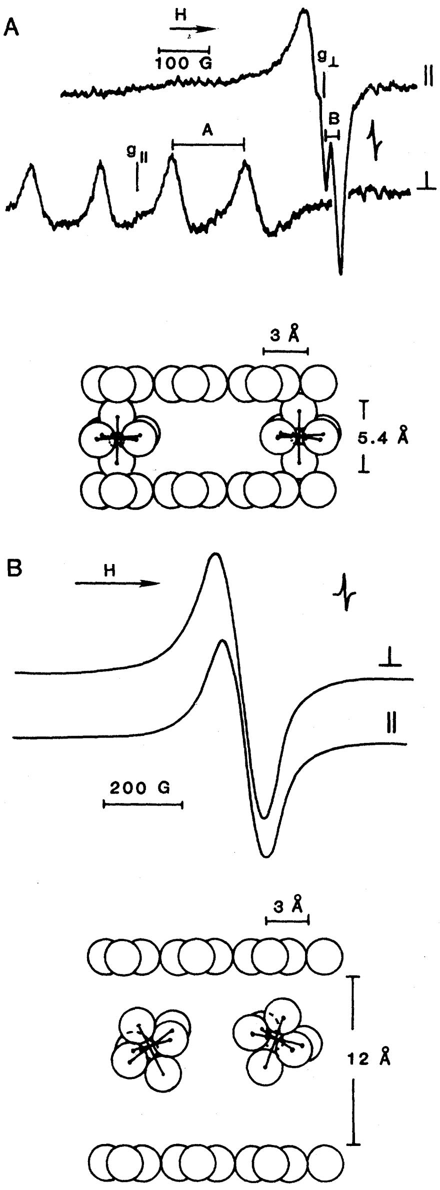


Fig. 2. Effect of interlayer swelling on the ESR spectra and dynamics of Cu(H$_2$O)$_6^{2+}$ ions in hectorite. (A) Resonance components $g_\perp$ and $g_\parallel$ observed for the ion under conditions where three layers of water occupy the interlayer and the C_4 axis is perpendicular to the silicate sheets. (B) Time-averaged spectra observed for the rapidly tumbling ion in interlayer solvated by five or six layers of water. Uncoordinated water molecules have been omitted for simplicity. Spectra labeled || and ⊥ have the applied magnetic field parallel and perpendicular, respectively, to the silicate layer.

As the smectite interlayers are swollen beyond the dimensions of the coordination sphere of the aquated metal ion, the complex becomes solvent-separated from the surface and begins to tumble rapidly. Also, under multilayer solvation conditions only the first one or two solvent molecular layers adjacent to the silicate surface exhibit significantly restricted motions (*40*).

Figure 2 illustrates the effect of interlayer swelling on the ESR spectra and dynamics of Cu^{2+} ions in an oriented film sample of hectorite. With three water layers occupying the interlayer region, the axially elongated Cu(H$_2$O)$_6{}^{2+}$ ion is oriented with the C_4 symmetry axis perpendicular to the silicate sheets, as judged from the spectral anisotropy (*41*). Swelling the interlayers to ~ 12 Å results in time-averaged spectra as the ion tumbles rapidly and undergoes dynamic Jahn-Teller distortions in the interlayer region. Quantitative estimates of the tumbling motion of Mn^{2+} and VO^{2+} ions under comparable swelling conditions show their correlation times to be only 30 to 50 percent larger than those observed for the same ions in dilute aqueous solution (*42, 43*). It is this labile nature of solvated smectite clay interlayers which makes possible their use as intercalation catalysts under mild reaction conditions.

Intercalated Metal Complex Catalysts

Although the importance of metal exchange cations in the acid-catalyzed reactions of smectites was revealed more than 40 years ago (*44*), it has been only recently that authentic metal complex–catalyzed reactions have been carried out in the interlamellar space of these minerals. Relatively few catalyzed reactions have been carried out to date (*45, 46*), yet they have revealed several general features of intercalated clay catalysts.

Surface chemical effects can greatly influence the specificity of an intercalated metal complex catalyst, particularly when two or more reaction pathways exist and the pathways are related by protonic equilibria. The importance of surface chemical effects is illustrated by the hydrogenation of terminal olefins with Rh(PPh$_3$)$_2{}^+$ as a catalyst precursor.

In this catalytic system, the reaction mechanism involves the formation of metal dihydride and monohydride intermediates which are in protonic equilibrium (*47*):

$$\mathrm{Rh(PPh_3)_2^+} \xrightarrow{\mathrm{H_2}} \mathrm{RhH_2(PPh_3)_2^+} \rightleftarrows \mathrm{RhH(PPh_3)_2} + \mathrm{H^+} \qquad (3)$$

The addition of olefin to the dihydride intermediate affords mainly hydrogenated product, whereas the reaction of olefin with the monohydride leads to undesirable substrate isomerization in addition to hydrogenation.

When the hydrogenation of 1-hexene is carried out with $\mathrm{Rh(PPh_3)_2^+}$ in homogeneous solution, the dihydride and monohydride reaction pathways both operate, and the hexane : 2-hexene product ratio is ~ 65:35, independent of conversion. However, the intercalation of $\mathrm{Rh(PPh_3)_2^+}$ in $\mathrm{Na^+}$-hectorite at the 10 percent exchange level can dramatically alter the extent of olefin isomerization (*48*). At the appropriate substrate concentration (> 0.7*M*) and water content of the methanol solvent (< 0.5 percent by weight), essentially quantitative conversions of 1-hexene to hexane can be achieved. More recent studies indicate that the hydrolysis of $\mathrm{Na^+}$ in the interlayer helps to shift the equilibrium in Eq. 3 in favor of the dihydride intermediate (*49*). Since the extent of $\mathrm{Na^+}$ hydrolysis is a sensitive function of the water content of the solvent and the substrate concentration, one can adjust these latter parameters to improve catalytic specificity, even though the homogeneous catalyst is insensitive to such factors.

It should be noted that neutral reaction intermediates formed by proton dissociation reactions analogous to Eq. 3 generally are undesirable, because the neutral species can desorb from the surface and be lost to solution. In these situations, desorption may be avoided by replacing one or more neutral ligands on the metal with a positively charged ligand. The phosphonium-phosphine ligand $[\mathrm{(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2(CH_2C_6H_5)^+}]$, abbreviated ($\mathrm{P\text{-}P^+}$), has been used in place of $\mathrm{PPh_3}$ to form complex catalysts of the type $\mathrm{RhH_2Cl(P\text{-}P^+)_x}$, which are positively charged analogs of Wilkinson-type complexes (*50*). This ligand also has been used successfully to immobilize rhodium hydroformylation catalysts in smectite clay interlayers (*45, 51*).

Under certain conditions of interlayer swelling, the size and shape of the substrate can be important factors in determining the selectivity of intercalated clay catalysts. The importance of substrate spatial factors is illustrated by the data in Table 2 for the hydrogenation of alkynes to the corresponding *cis* alkenes with $\mathrm{Rh(PPh_3)_2^+}$ under homogeneous and intercalated reaction conditions (*48*). As the size of the R group on either side of the C≡C bond increases from 1-hexyne to diphenylacetylene, the relative reaction rates for the intercalated and homogeneous catalysts ($R_\mathrm{I}/R_\mathrm{H}$) decrease dramatically. Also, the reactivity of the intercalated catalyst toward a given alkyne decreases greatly with decreasing interlayer swelling, as illustrated by the $R_\mathrm{I}/R_\mathrm{H}$ values in Table 3 for 2-decyne reduction in solvents of different swelling power.

Although the results for alkyne hydrogenation show that the selectivity of the intercalated catalyst depends on substrate size and interlayer spacing, a molecular sieving effect is precluded by the data in Table 2. Each substrate in the table is sufficiently small in at least one dimension to penetrate the methanol solvated interlayers, which are ~ 7.7 Å thick. The apparent substrate size selectivity arises instead from the spatial requirements of partially oriented $\mathrm{RhH_2(PPh_3)_2^+}$-alkyne intermediates in the restricted interlayer region. One possible orientation is illustrated in Fig. 3A. Destabilization of the oriented intermediate due to unfavorable repulsions between the silicate layers and R groups on the substrate will be especially severe when the substrate critical dimension, defined in Fig. 3B, is larger than the interlayer swelling. However, a precise relation between substrate critical dimension, interlayer swelling, and reactivity cannot be expected. In addition to being turbostratic, clays interlayered with metal complex catalysts tend to be interstratified, with some interlayers somewhat larger or smaller than the average value indicated by the observed 00*l* x-ray reflections (*52*). Thus, efficient catalytic discrimination among substrates on the basis of size or shape can be expected only when the differences in critical dimensions are larger than the spread in interlayer spacings.

Table 2. Hydrogenation of alkynes in methanol at 25°C with intercalated and homogeneous $\mathrm{Rh(PPh_3)_n^+}$ catalyst precursors. Substrate concentration is 1.0*M*; substrate: Rh = 2000:1. Rates are expressed in milliliters of H_2 per minute per millimole of Rh. Catalyst intercalated in $\mathrm{Na^+}$-hectorite at a loading of 0.72 percent Rh by weight. The last column shows the ratio of intercalated to homogeneous rates.

Substrate	Initial rate		$R_\mathrm{I}/R_\mathrm{H}$
	Intercalated	Homogeneous	
1-Hexyne	2100	2100	1.0
2-Hexyne	2200	2400	0.92
2-Decyne	1200	2500	0.48
3-Hexyne	360	1800	0.20
PhC≡CPh	< 1	100	< 0.01

Table 3. Hydrogenation of 2-decyne with intercalated and homogeneous $\mathrm{Rh(PPh_3)_n^+}$ in solvents of different swelling power. The value Δd_{001} is the average interlayer thickness of the solvated intercalate as determined from 001 x-ray reflections. The other parameters are defined in the legend of Table 2.

Solvent	Initial rate		$R_\mathrm{I}/R_\mathrm{H}$	Δd_{001} (Å)
	Intercalated	Homogeneous		
CH_2Cl_2*	2800	3300	0.85	10.0
MeOH	1200	2800	0.43	7.7
Et_2O/MeOH (3:1 by volume)	660	2800	0.24	6.7
C_6H_6*	20	1000	0.02	5.7

*These solvents contain 7 percent methanol by volume.

Another intercalated system that exhibits favorable deviations from solution behavior is the overall 1,2 and 1,4 addition of hydrogen to 1,3-butadiene derivatives in the interlayer region of $\mathrm{Rh(NBD)(dppe)^+}$-hectorite, where NBD is norbornadiene, and dppe is 1,2-bis(diphenylphosphino)ethane (*53*). With methanol or acetone as swelling solvents, the yields of terminal olefin obtained by 1,2 addition are 1.5 to 2.3 times larger than those obtained under homogeneous reaction conditions. Moreover, the enhanced specificity toward terminal alkenes occurs at the expense of the less desirable internal alkene products (1,4 addition). No reaction is observed in benzene, which fails to swell the interlayers. It has been suggested that the effect of intercalation on the distribution of kinetically regulated products may result in part from the surface-induced polarization of C–C bonds in the metal-allyl intermediates. That is, factors more subtle than surface chemical equilibria or spatial requirements may influence the energies of reaction pathways in clay interlayer.

Although the discussion thus far has focused on the factors that influence the reactivity and selectivity of metal complex catalysts in smectite clay interlayers, some catalytic systems do show very similar selectivities under intercalated and homogeneous reaction conditions. For example, the hydroformylation of 1-hexene in acetone (100°C, CO:H_2 = 1:1; total pressure, 600 pounds per square inch) with clay intercalated $RhH(CO)_x(P\text{-}P^+)_2$ complexes affords *n*-heptanal and 2-methylhexanal in ratios of 3:1 (*45, 51*). With the same catalyst system under homogeneous reaction conditions the ratio of normal to branched-chain aldehydes is ~ 2:1. The small difference in product ratios suggests that the intercalated intermediates leading to normal and branched-chain aldehydes have approximately the same relative stabilities as in solution. X-ray diffraction studies indicate that the interlayers occupied by the metal complexes are swollen by acetone to a thickness of ~ 15 Å. Apparently, at this level of swelling steric factors, surface polarization effects, or solvation effects do not alter significantly the relative energies of reaction pathways leading to aldehydes, and solution-like product distributions are observed. That reaction occurs in the interlayers of the clay and not at external sites is verified by the absence of hydroformylation in benzene, which fails to swell the interlayers.

Also, the asymmetric synthesis of certain α-aminoacrylates can be achieved with chiral rhodium complexes immobilized in smectite interlayers without sacrificing the high optical yields typified by the same complexes under homogeneous conditions (*45, 54*). For example, the chiral precursor to the drug L-dopa can be synthesized in 95.1 percent optical yield from the corresponding α-acetylaminoacrylic acid by hydrogenation in 95 percent ethanol in the presence of $Rh[(R)\text{-}4\text{-}Me\text{-}Prophos]^+$-montmorillonite, where 4-Me-Prophos is the dissymmetric bidentate ligand $(CH_3C_6H_4)_2PCH(CH_3)CH_2P(C_6H_4CH_3)_2$ (*45, 54*). The optical yield obtained with the homogeneous catalyst under the same reaction conditions (25°C, 1 atmosphere) is 95.3 percent. The advantage of the intercalated clay catalyst, of course, is that it can be readily recovered by filtration from the reaction products and recycled.

J. M. Thomas and co-workers have reported a number of proton-assisted reactions of organic molecules with smectite clays containing acidic aquocations. Under the reaction temperatures generally utilized (100° to 200°C), one or at most two partial molecular layers of water occupy the interlamellar region of the mineral. Although the interlayers are highly restricted, organic molecules apparently are capable of penetrating the interlayers at the monolayer level. Direct evidence for interlamellar reaction has been demonstrated for the quantitative reaction of water in the one- and two-layer hydrates of Cu^{2+}-montmorillonite with C_6 to C_8 terminal alkenes to form almost exclusively 2,2′-dialkyl ethers (*55*). Although this particular reaction is not self-sustaining and therefore not genuinely catalytic, it illustrates the remarkable selectivity that can result from reaction pairs in close proximity on the interlayer surfaces. Recent studies by Adams *et al.* (*56*) suggest that ether production results from reaction between a secondary alcohol formed in a water-rich region of the interlayer (for instance, near Cu^{2+} ions) and a nearby carbocation formed in a local environment low in water.

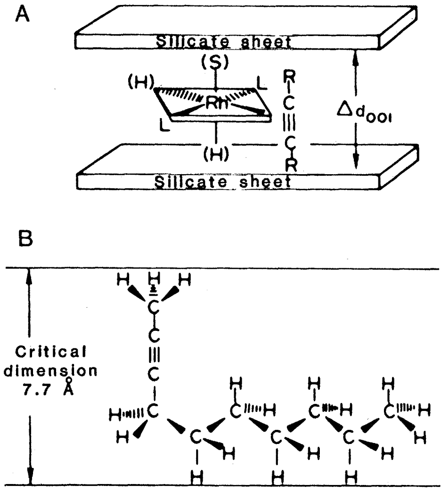
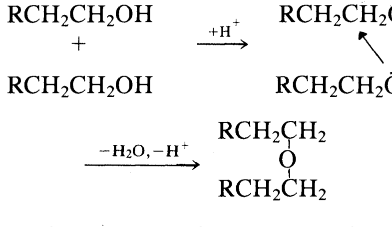


Fig. 3. (A) Proposed orientation for the reactive $RhH_2L_2^+$-alkyne intermediate formed in the interlayers of hectorite. Note that the C≡C axis is orthogonal to both the L–Rh–L axis and the plane of the silicate sheets. (B) The 2-decyne critical dimension, defined as the minimum interlayer distance that must be spanned by the substrate to achieve a reactive configuration.

The dehydration of primary alcohols over Al^{3+}-montmorillonite at 200°C has been shown to yield 1,1′-dialkyl ethers in high yields (*57*). In this case the reaction is truly catalytic, and the clay can be reused. Remarkably, little or no intramolecular alcohol dehydration to alkenes is observed. The dehydration mechanism apparently proceeds by nucleophilic displacement of water from adjacent reactant pairs on the silicate surfaces:



$$\begin{array}{c} RCH_2CH_2OH \\ + \\ RCH_2CH_2OH \end{array} \xrightarrow{+H^+} \begin{array}{c} RCH_2CH_2\overset{+}{O}H_2 \\ \nwarrow \\ RCH_2CH_2\ddot{O}H \end{array} \xrightarrow{-H_2O,\,-H^+} \begin{array}{c} RCH_2CH_2 \\ | \\ O \\ | \\ RCH_2CH_2 \end{array} \qquad (4)$$

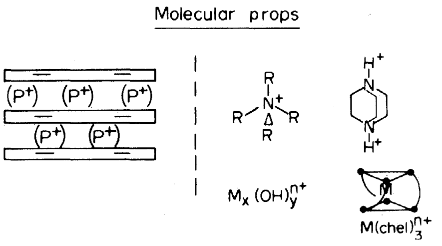
Analogous catalytic transformations occur in the conversion of thiols to dialkyl sulfides (*58*) and in the formation of secondary amines from primary amines (*59*) on acidic metal ion exchange forms of montmorillonite. The absence of branched Markovnikov products in all of these reactions precludes the intermediacy of carbocations or alkenes. Extensive alkene formation is observed, however, for the dehydration of secondary and tertiary alcohols on montmorillonite (*57*).

The catalytic addition of carboxylic acids to alkenes on Al^{3+}-montmorillonite at 200°C also is highly specific (*60*). Ethyl acetate and propyl acetate are the sole products formed from the addition of acetic acid to ethylene and propylene, respectively. In this case the reaction proceeds through equilibrated carbocation intermediates, as evidenced by the distribution of Markovnikov addition products obtained in the reaction of acetic acid and 1-hexene.

The catalytic importance of reactant pair proximity in the interlayers of smectite clays was demonstrated incisively by Weiss (*15*) in his studies of oleic acid oligomerization in $N(CH_3)_4^+$-montmorillonites of differing average charge density. The yield of desired dimeric acid is found to be a maximum (66 percent) when the average layer charge is ~ 0.56*e* per Si_8O_{20}. At this value the average distance between $N(CH_3)_4^+$ ions in the interlayers permits optimum pairing of oleic acid molecules. As the distance between exchange cations is decreased with increasing layer charge, the number of reacting pairs is decreased by the intervening cations. Consequently, *cis-trans* isomerization and H-transfer reactions of the monomer compete more favorably with the dimerization reaction. Decreasing the layer charge density below 0.56*e* per Si_8O_{20} increases the number of three- and four-monomer groupings in the space between exchange cations, and higher oligomers are formed at the expense of dimers. Significantly, no oligomerization is observed for the corresponding C_{18} alcohol and nitrile, which adopt vertical or inclined positions in the interlayer rather than the parallel orientation assumed by the carboxylic acid.

Pillared Clays

Interlamellar reactions in ordinary metal ion exchange forms of smectite clays at high temperatures (> 200°C) are precluded by the dehydration and collapse of the interlayer region. The limitations imposed by interlayer collapse have recently been circumvented by the intercalation of thermally stable, robust cations which act as molecular props or pillars, keeping the silicate layers separated in the absence of a swelling solvent. As illustrated in Fig. 4, various types of cations have been used as pillar-



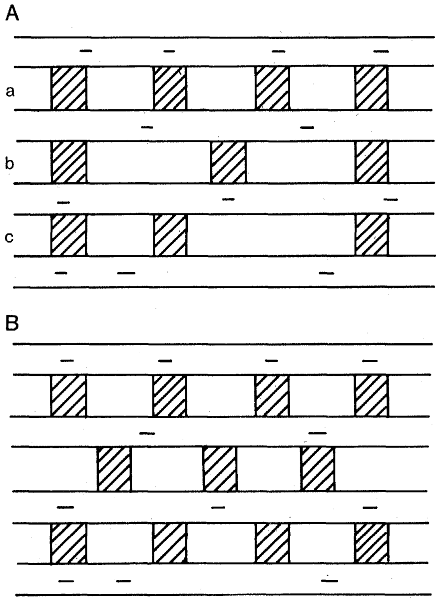


Fig. 4 (left). Schematic representation of a pillared clay. The pillaring agent (P^+) may be an alkylammoniun ion, a bicyclic amine cation, a *tris* metal chelate (for instance, M = Fe^{2+} and chel = 1,10-phenanthrolein), or a polynuclear hydroxy metal ion [for instance, $Al_{13}O_4(OH)_{28}^{3+}$]. The regions between pillaring cations define pores for adsorption and possible catalysis of organic molecules. Fig. 5 (right). (A) Irregular and (B) regular distribution of pillaring cations in clay interlayers. Irregular spacings from interlayer to interlayer (a and b) and within an interlayer (c) are expected when the pillaring cations are stable to hydrolysis [for instance, NR_4^+ or $M(chel)_3^{2+}$] and the surface concentration of cations is determined by the nonuniform charge density on the layers. Regular spacing of pillars becomes possible when hydrated hydroxy cations [such as $(Al_{13}O_4(OH)_{28+n}^{(3-n)+}$] are more or less uniformly adsorbed on the interlayer surfaces. In the latter case the average charge per pillaring cation varies with the extent of hydrolysis and the negative charge density of the clay layers.

ing agents, including alkylammonium ions (*61*), bicyclic amine cations (*62, 63*), metal chelate complexes (*64, 65*), and polynuclear hydroxy metal cations (*66, 67*).

The concept of pillaring smectite clays was demonstrated more than 25 years ago by Barrer and MacLeod (*68*) when they utilized tetraalkylammonium ions to induce interlayer porosity in montmorillonite. Although Barrer (*61*) further developed the chemistry of alkylammonium clays, and even demonstrated their selective adsorption properties, the idea of pillaring clays to achieve porous networks was overshadowed by the rapid advances being made in the synthesis and catalytic applications of zeolites. There is now renewed interest in pillared clays, because it is realized that their pore sizes can be made larger than those of faujasitic zeolites. Moreover, by varying the size of the pillar or the spacing between pillars, or both, one may adjust the pore size to suit a particular application. Thus pillared clays offer new possibilities for catalysis of larger molecules such as those found in residual crude oils.

Among the pillaring agents illustrated in Fig. 4, the alkylammonium and bicyclic amine cations decompose below 250°C and the metal chelates degrade below 450°C (*69*). However, at least two polynuclear hydroxy cations afford pillared phases that are stable above 500°C. Brindley and his co-workers (*66, 67*) were first to report that hydroxy aluminum and hydroxy zirconium cations formed by hydrolysis over a specific range of OH^-/M^{n+} values yielded thermally stable clays with surface areas of 200 to 500 m^2/g and interlayer free spacings near 9 Å. Using similar methods of preparation, Lahav *et al.* (*70*) and Vaughan and Lussier (*71*) independently prepared analogous pillared phases containing hydroxy aluminum ions.

The hydroxy zirconium pillar is a Zr_4 oligomer of the type $Zr_4(OH)_{16-x}^{x+}$ (*67*). Although Al_6 oligocations have been proposed as the intercalated species in the hydroxy aluminum system (*66, 70*), the structure of the pillaring cations most likely is an Al_{13} oligomer related to the known cation $Al_{13}O_4(OH)_{24}^{7+}$ (*71, 72*). A recent evaluation of ^{27}Al NMR and potentiometric titration data for hydrolyzed solutions of Al^{3+} indicate that $Al_{13}O_4(OH)_{28}^{3+}$ is the dominant species in solution at the OH^-/Al^{3+} ratios used to prepare hydroxy aluminum pillared clays (*73*). Also, the interlayer free spacing (~ 9.5 Å) of smectites interlayered with hydroxy aluminum are consistent with the expected size of an Al_{13} oligomer.

The remarkable thermal stability of the Zr_4 and Al_{13} pillared smectites has been attributed to the formation of metal oxide clusters upon dehydroxylation of the hydroxy cations at elevated temperature. In the case of Al_{13}-montmorillonite, the overall interlayer reaction may be written as

$$\underline{\overline{Al_{13}O_4(OH)_{28+n}^{(3-n)+}}} \xrightarrow{-H_2O} \underline{\overline{6.5\ Al_2O_3\ +\ (3-n)H^+}} \qquad (5)$$

where the alumina is in the form of small clusters. Little is known at present about the structure of the clusters or the location of the protons in the intercalate.

Shabtai (*74–76*) and Vaughan and coworkers (*77, 78*) independently disclosed the molecular sieving and acid catalytic properties of clays pillared by hydroxyl metal ions. For example, Al_{13}- and Zr_4-montmorillonites, when used as petroleum cracking catalysts, give gasoline octane ratings comparable to zeolite catalysts, along with enhanced yields of light-cycle oils (furnace oil and diesel fuel) (*77*). Also, Al_{13}-montmorillonite adsorbs molecules as large as mesitylene, but not isodurene, which have kinetic diameters of 7.6 and 8.0 Å, respectively (*77*).

The highly selective molecular sieving properties of clays pillared by hydroxy metal cations require a regular distribution of pillars and pores in the interlayer region. However, the layer charge distribution in smectite clays is highly irregular (*79–81*), varying by as much as a factor of 2 from interlayer to interlayer (*81*). Thus one should expect a nonuniform distribution of pillars and a range of pore sizes, particularly for intercalates containing hydrolytically stable pillaring agents such as $M(chel)_3^{n+}$, where ion exchange is the sole driving force for intercalation (Fig. 5A). With polynuclear hydroxyl metal pillars, however, the ions apparently fill each interlayer region to essentially the same population density, regardless of the layer charge (*66*) (Fig. 5B). In the latter case, the pillar spacing appears to be decided by the radius of the hydrated cations, and the charge on the cations is regulated by the extent of hydrolysis, which is dependent on layer charge. Thus a suite of Al_{13}-smectites with cation exchange capacities in the range 60 to 120 mEq per 100 g exhibit essentially the same nitrogen, benzene, and neopentane surface areas.

Although polynuclear hydroxy metal ions formed by hydrolysis in aqueous solution can yield pillared clays with interlayer free spacings in the range 5 to 20 Å, the number of metals that form suitable oligomeric species is limited. New approaches to the pillaring of smectite clays promise to extend the number of pillaring species. It has been possible, for example, to interlayer montmorillonite with silicic acid by hydrolysis of silicon acetylacetonate cations in the interlayer region (*82, 83*):

$$\underline{\overline{Si(acac)_3^+}} \xrightarrow[-H(acac)]{H_2O} \underline{\overline{Si(OH)_4\ +\ H^+}} \qquad (6)$$

The silicic acid–clay complex has an interlayer free spacing of ~ 3 Å and a nitrogen surface area of ~ 200 m^2/g after heating to 550°C. Also, a related approach involving hydrolysis and oxidation of metal cluster cations such as $Nb_6Cl_{12}^{2+}$ and $Ta_6Cl_{12}^{2+}$ affords clays pillared by small clusters of metal oxide approximately 10 Å in diameter and stable to ~ 400°C (*84*):

$$\overline{\underline{Nb_6Cl_{12}^{2+}}} \xrightarrow[-HCl,\ -H_2]{H_2O} \overline{\underline{3Nb_2O_5 + 2H^+}} \qquad (7)$$

Conclusion

This discussion has indicated the novel properties of smectite clay intercalates from the viewpoint of catalysis. There are, of course, limitations to the use of smectite clays as catalysts. In particular, their compositional variability, hydrolytic instability (particularly at high and low *p*H values), and resistance to fluid flow under certain conditions of aggregation can impose important constraints on their utility. Nevertheless, research on the intercalation chemistry of smectites is gaining momentum rapidly, and we can look forward with confidence to new developments which will broaden our ability to transform these abundant minerals into new classes of selective heterogeneous catalysts.

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85. Support from the National Science Foundation is gratefully acknowledged. Also, I wish to acknowledge the contributions of my former students and colleagues whose names appear in the references cited.