

1985 GEORGE W. BRINDLEY LECTURE

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INTERNAL SURFACE OF CLAYS AND CONSTRAINED CHEMICAL REACTIONS

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INTRODUCTION

At the 1981 International Clay Conference in Bologna and Pavia, Italy, Professor G. W. Brindley was asked to deliver a general lecture entitled "The Teaching of Clay Mineralogy." Figure 1 reproduces the only slide that was used to illustrate this lecture (Brindley, 1982). The figure is used here not only to recall the world of George Brindley, but to delineate the subject of the present paper. Although the present paper will touch briefly on several of the subjects listed in the figure, it will concentrate on only one aspect of the field—the physical and chemical processes that occur in the interlayer space of swelling clays. Because of limited space, it will not discuss experimental methods, despite the many recent discoveries that have been possible as a result of the extraordinary development of such techniques in recent years.

The present paper will, however, show that knowledge of some of the physical and chemical processes occurring in smectite clays has contributed in a very respectable way to the overall progress of science. Although the fundamental importance of clays and clay-mineral reactions is now well recognized in many chemistry and physics departments, 25 years ago it was difficult to find a chemistry department that considered "muds" to be a respectable reagent for research! Practically all investigations of such muds were conducted in soil departments and in a few geochemical laboratories. It is intellectually stimulating to search for the reasons for such changes in attitude to that we might be better able to predict areas of future breakthrough.

One of the chief reasons for the current interest in clay minerals is that the study of intercalation compounds has opened new fields of research. The modifications of the electronic and magnetic properties of structures, such as those of graphite, chalcogenides, and transition metal oxides, by the intercalation of alkalis, alkaline earths, and even hydrogen are so extensive that intercalation compounds are now standard items in many materials science laboratories. Because of their unique structures, phyllosilicates offer the potential to synthesize other types of intercalation compounds, and it is not too far fetched to predict that synthetic clays containing exotic tetrahedral and/or octahedral cations will eventually be prepared that will react in new and different ways with carefully chosen intercalation agents.

A second reason for the increased attention being paid to clay minerals is the growing importance of catalysis in a world in which energy resources are becoming less abundant and more expensive. In the Houdry process, for example, clay is a vital raw material. The enormous success that has been achieved in the field of catalysis by molecular sieve zeolites has stimulated inorganic chemists to develop sophisticated ways of using clays as catalysts, for example, by propping the sheets of expandable clays apart. This is a challenging field and will be discussed at length below.

A third reason for the growing activity in the field of clay mineral reactions is the renewal of interest in their role in colloid science. Clays in the natural state or modified by surfactants have the potential to produce novel colloidal systems in which supramolecular

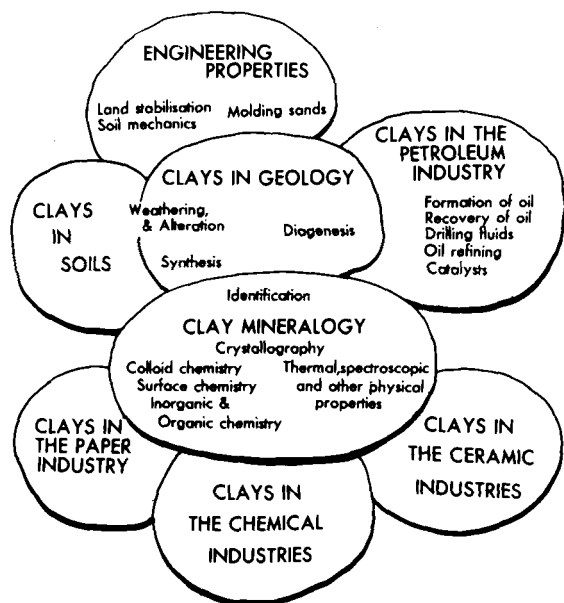


Figure 1. The world of G. W. Brindley (Brindley, 1982).

organizations can be formed. Such complex systems show much higher efficiency for certain chemical processes, for example, by decreasing the probability of back reactions.

The outline of the clay-mineral reactions to be reviewed in this paper, shown in Figure 2, has been constructed in such a manner to emphasize the roles of the three principal characteristics of smectite clays: their electrical charge, their internal pore space, and their large surface area.

CLAYS AS SOLID STATE SYSTEMS

A homoionic clay is essentially a salt that consists of a polyanion of infinite radius of curvature and exchangeable cations. Therefore, the screening of the cationic charge is much less than it is, for example, in zeolites. In partially dehydrated clays, one consequence of the strong electrical field near the cation is the large degree of dissociation of coordinated water (Mortland, 1968). A pronounced preferential orientation of adsorbate with respect to the symmetry axis of the host structure (which is perpendicular to the adsorbing surface) has been observed not only if the adsorbate is a ligand of the charge-balancing cation, but also for some positively charged moieties in the interlayer position. Many examples are known; among the first to be documented was the orientation of pyridinium (Serratosa, 1966), and among the most recent is the orientation of tetrathiafulvalene, a strong electron donor, which is well known in the field of charge-transfer chemistry (Van Damme *et al.*, 1984b). Ligand exchange reactions in the interlayer space may take advantage of the fact that oxygen atoms of the partly covalent-partly ionic

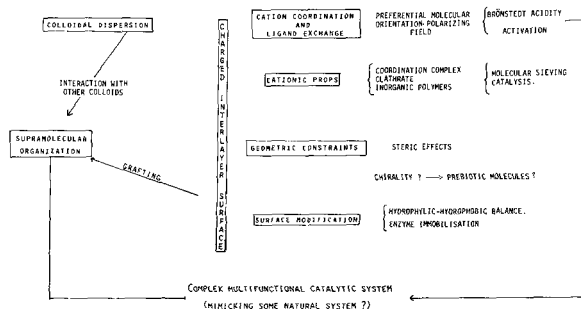


Figure 2. Schematic diagram illustrating chemical reactions constrained to the interlayer space of clay minerals.

structure can complete the coordination shell of the metal ion. Copper and cobalt complexes, however, behave differently from one another in this regard (Schoonheydt and Pelgrims, 1983).

A subject that deserves more attention is the influence of location of the cationic substitution on the physical and chemical properties of the ligands coordinated to the charge-balancing cations. Chourabi and Fripiat (1981) showed that the symmetry of the NH_4^+ cation in beidellite is C_{3v} instead of T_d . More recently, Casal *et al.* (1984) provided similar evidence for altered symmetry in the NH_4^+ -clathrate of a 6-oxygen-ring crown-ether adsorbed by montmorillonite. In these materials, but for different reasons, the field acting on the NH_4^+ probe is apparently axially symmetric.

The location of the cationic substitution is particularly important for acid catalysis. The Brönsted acidity in a clay without tetrahedral substitution is due mostly to the enhanced degree of dissociation of water or to the hydrolysis of acid cations (e.g., $\text{Al}(\text{H}_2\text{O})_6^{3+}$). Many acid-catalyzed reactions have been reported during the last 20 years; Thomas (1982) and Ballantine (1986) in particular discussed impressive lists of reactions that have been carried out in this manner.

Heating an acid beidellite to 300°C gives rise to an Al-OH-Si linkage which is responsible for superacidity (Schutz *et al.*, 1986). This source of acidity has the advantage of being stable at high temperatures if collapse of the interlayer space can be prevented. Maintaining a reasonably large interlayer spacing at temperatures higher than the dehydration temperature has remained a challenge for many years. Brindley and Sempel (1977) and Lahav *et al.* (1978) used hydroxy-aluminum polymers, which are positively charged and which can be cation-exchanged on montmorillonite, to prevent collapse. Vaughan and Luissier (1980) and Pinnavaia (1983) advocated propping the layers apart by intercalating a "Keggin" cation (Al_{13}) containing 12 alumina octahedra coordinated to one aluminate tetrahedron. Recently, Plee *et al.* (1985) verified the formation of such a "propped" montmorillonite. Mortland and Berkheiser (1976) and Shabtai *et al.* (1977)

also prepared pillared clays using large protonated molecules, such as Dabco (1,4 diazobicyclo (2,2,2)-octane) (see also, Loeppert *et al.*, 1979). Surface areas of ~ 300 m²/g measured by N₂ adsorption (BET method) were obtained with Dabco (2+ and 1+ cations) (see, e.g., Van Leemput *et al.*, 1983), whereas the observed d(001) value was only 14.5 Å. Similar surface areas have been measured for clays pillared with the Al₁₃ hydroxy-Al-polymer, despite the fact that the 001 spacing of this material is ~ 18 Å. This result is puzzling unless a free space of $\sim 18 - 9.6 = 8.4$ Å does not allow a double layer of physisorbed N₂ molecules to form in the interlayer. Neither the diameter of the dinitrogen molecule nor the surface roughness seem to provide an adequate explanation for the discrepancy in surface areas measured for these two pillared clays (Van Damme and Fripiat, 1985).

Pillaring with organic props does not lead to thermally stable materials, but thermal stability is not the paramount property if molecular sieving is the main objective, as emphasized by Barrer (1978). The situation is different if the pillared material is to be used as a catalyst support. From the catalyst point of view, other avenues of approach must be explored. Pillaring with oxides which have specific catalytic properties of their own could lead to useful materials; however, few inorganic polymers are known that can be used to produce thermally stable pillars.

GEOMETRIC CONSTRAINTS

The geometric constraints of the interlayer may favor the adsorption and chemical stability of a steric isomer. For example, the pseudooctahedral [Ru(bpy)₂(H₂O)₂]²⁺ complex exists as a *trans* isomer (in which water molecules occupy opposite corners of the pseudooctahedron) or a *cis* isomer (in which the two water molecules exist at vicinal corners). In acidic solution, the *cis-trans* isomerization is induced by light, whereas the *trans-cis* isomerization is a thermally activated dark reaction. Both *cis* and *trans* isomers are readily adsorbed from solution by a clay film, but irrespective of the isomeric state in solution, the *trans* isomer is the only type present on the clay at high contents of hydration water ($\sim 15\%$ w/w). The *cis* isomer is stable at a hydration-water content of $\sim 2.5\%$ w/w (Cruz *et al.*, 1982). The conversion is a room-temperature dark reaction. This behavior must be due to a much lower activation barrier between the two ground states in the interlamellar space, but the mechanism is unclear. The *cis* isomer contains two planar bipyridyl ligands parallel to the (001) lattice plane, whereas in the *trans* isomer, the ligands are tilted with respect to the *c* axis. In the *cis* orientation, the two water molecules are able to interact with the surface oxygens, whereas in the *trans* orientation, this interaction is weaker. In the *cis* isomer the hydrophobic and hydrophilic regions of the molecule are farther apart

than in the *trans* isomer. Inasmuch as greater hydration favors the *trans* isomer relative to the *cis* form, the balance between the hydrophobic and hydrophilic interactions together with swelling and squeezing ($d(001) = 7.8$ Å for the *trans* form, 6.5 Å for the *cis* form) of the interlayer space may be responsible for the small energy difference between the ground levels in the adsorbed state.

Another interesting reaction in which steric constraints are evidently important is the photoaquation of Cr(bpy)₃³⁺ into *cis*-Cr(bpy)₂³⁺(H₂O)₂ (Abdo *et al.*, 1981). Here, the trisbipyridyl complex is oriented with respect to the clay layer in such a way that two of the three ligands are parallel to the (001) plane. Such an orientation favors not only the removal of the third tilted ligand and the formation of the *cis*-diaquo form, but also allows the reaction to be partially reversible in the dark. Reversibility is not observed in solution. The use of clay films as supports for such photo-induced reactions was reviewed recently by Van Damme *et al.* (1984a).

One very important topic which deserves more investigation is that of chiral reactions carried out in the interlayer space, such as the asymmetric hydrogenation of prochiral olefins using cationic Rh complexes (Mazzei *et al.*, 1980). The chemistry of these complexes was studied by Schoonheydt *et al.* (1984). With respect to the possible role of clays in inducing chirality in molecules, many experimentalists have tried to use clays as catalysts (or templates) for the synthesis of prebiotic molecules. Proof for the synthesis of optical isomers, however, or even for the preferential adsorption of one optically active component, has not yet been presented. Without clear evidence that clays have the ability to generate or concentrate optically active compounds, this author is pessimistic about the importance of clays in explaining chirality in the prebiotic environment.

SURFACE MODIFICATION

Scientific activity in the area of oil recovery has been instrumental in promoting research dealing with the adsorption of surfactants by rock components—clay minerals in particular. This domain of research has been in part responsible for the recent interest in obtaining quantitative estimates of hydrophobicity and hydrophilicity.

In the 1960s, the use of functionalized silanes made possible the transformation of hydrophilic surfaces into strongly hydrophobic ones by the formation of covalent links between an organic group and the inorganic surface. The effectiveness of surfactants in surface modification is due either to van der Waals interaction of the surface with polar segments of large molecular species (e.g., polyethoxy) or to the electrostatic interaction with cationic (or anionic) heads of molecules with long hydrophobic tails. The possibilities for modifying surface properties in this manner are endless,

inasmuch as a subtle balance between the hydrophilic and hydrophobic parts can be tailored and surface charge can be modified. The versatility of smectites (bentonites) in a wide range of applications has been based on this balance of surface properties. More work is needed in this area. For example, the relationships between the dynamic properties of slurries (e.g., viscosity) and the extent of hydrophobic character are still entirely empirical.

Another related area of research which shows promise is that of enzyme immobilization by clays. Here also, hydrophobic and ionic modes of binding may compete. For example, Garwood *et al.* (1983) studied the adsorption of glucose oxidase on the external surface of hexadecyltrimethylammonium-montmorillonite. The pH for optimum activity was similar for the immobilized and free forms of the enzyme. In contrast, Na-montmorillonite bound the active form of glucose oxidase by an ionic intercalation mechanism at pHs less than the isoelectric point of the enzyme. The 001 basal spacing at maximum adsorption (~ 35 Å) suggests an uncoiling and denaturation of the enzyme. In fact, ionic binding involved the protonated form of the enzyme, and the difference between the local pH and the isoelectric point determined the chemical driving force of the denaturation process. This process of uncoiling was not noted for hydrophobic immobilization, but the improvement in enzyme properties was obtained at the expense of available surface area, because hydrophobicity precluded clay swelling. Hydrophobic fixation, however, was the preferred bonding mechanism, because 50% of the enzyme activity was retained, whereas only 10% of the enzyme was active when it was bound electrostatically to Na-montmorillonite. On the other hand, Theng (1979) referred to examples of intercalation of enzymes with retention of catalytic activity.

At a more general level, surface modifications and colloidal properties are intimately related, and from that point of view it is useful to consider briefly some particular features of colloidal dispersions of smectites. Excluding the special case of extremely dilute suspension (0.1% w/w) of very fine fractions (< 0.2 μm) of Li-montmorillonite, small-angle X-ray scattering (Pons *et al.*, 1981) and nuclear magnetic resonance (NMR), Fripiat *et al.* (1982) have recently provided concurring evidence that most smectite particles are associated in tactoids. This evidence does not reconcile with the "card-house" model of particle association (van Olphen, 1977); instead it suggests behavior consistent with the findings of Tessier and Pedro (1982) who showed scanning electron micrographs of dominant face-to-face associations. Nevertheless, this apparent agreement between techniques hides serious discrepancies. Based on NMR data on a 2- μm Na⁺-hectorite suspension (clay: water ratios = 0.001 to 0.18), the average external surface area was estimated to be 80

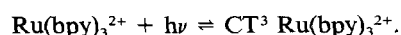
m²/g and found to be independent of the clay: water ratio. In contrast, small-angle X-ray scattering led to the conclusion that in very dilute sols, most of the layers are separated by distances of ~ 100 Å, whereas at clay: water ratios of ~ 0.3 , tactoids with internal separations of ~ 35 Å began to form. This aggregation should have increased the actual surface area detected by the NMR probe (H₂O) or D₂O) by a readily measurable quantity.

Van Damme *et al.* (1985) proposed a solution to this discrepancy by considering a fractal aggregation model. A two-dimensional diffusion-limited aggregation model of anisotropic particles having an anisotropy ratio of $\sim 1:9$ revealed that an aggregate of $n = 10^3$ platelets still had the same aspect ratio as the platelet from which it formed. More importantly, the model showed that the specific perimeter of the aggregate (in two dimensions) rapidly reached a constant value as n increased. In three dimensions, this corresponds to a constant external surface. Moreover, the interference function of an X-ray beam with these tactoids showed maxima which were related, not to an actual average distance between adjacent layers, but to a distribution of inter-sheet distances. Alcover *et al.* (1985) recently discussed this type of model.

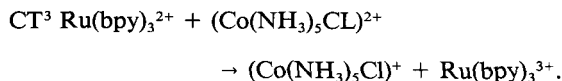
SUPRAMOLECULAR ORGANIZATION

In an ideal catalysis system, it is preferable to organize chemical functions to achieve either parallel or sequential chemical reactions while minimizing undesired processes. In molecules such as amino-acids, basic and acidic groups coexist, and both can function according to their nature without much interference. On a surface, a distribution of basic and acidic catalytic centers is easily visualized. The coexistence of two redox couples is more difficult to visualize because of fast and undesired electron transfer within a molecular framework. This kind of problem may be solved, at least theoretically, by adjusting the average distance between the reacting species depending upon kinetics of electron transfer. For example, consider an electron transfer in colloidal suspension from a positive to a negative coordination complex near a negative surface. After transfer, the positive complex will be more strongly adsorbed and the negative complex more strongly repulsed by the surface. This increase in the average distance between the donor and the acceptor reduces the back reaction.

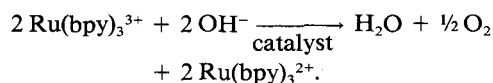
The following example illustrates a primitive system in which this idea is applied. Consider the "sacrificial" cycle of reactions which allow the photooxidation of water. The photosensitizer triggering the reactions is the well-known coordination complex Ru(bpy)₃²⁺, which, upon adsorption of a photon at 460 nm, is excited into the so-called CT³ state:



In this state the excited complex has a redox potential which promotes the transfer of an electron to cobalt(III) chloropentamine, which is in turn reduced into an unstable cobalt complex:



The fast decomposition of the Co(II) complex (which is sacrificed) inhibits the back-electron transfer reaction which would return the photosensitizer to its ground state. The Ru(III) complex has an adequate redox potential to react with the OH^- from the electrolytic dissociation of water, thereby producing molecular oxygen in the presence of the catalyst:



This sequence of reactions could be carried out in a clay slurry; the two coordination complexes are cation exchangers (e.g., 2% clay-water slurry having 10% of the cation-exchange capacity occupied by the ruthenium complex and 90% by the cobalt chloropentamine). The efficiency of RuO_2 as the catalyst for the water-dissociation reaction is well documented. A suspension of 500-Å diameter particles can be prepared easily and added to a solution of $\text{Ru}(\text{bpy})_3^{2+}$ and $(\text{Co}(\text{NH}_3)_5\text{Cl})^{2+}$. Photooxidation of water would then be obtained with visible light until $(\text{Co}(\text{NH}_3)_5\text{Cl})^{2+}$ was totally consumed (Lehn *et al.*, 1979). There is apparently no reason why, by adjusting the pH, colloidal RuO_2 could not catalyze the same reaction in the clay slurry. The reaction should be even faster because the reacting species are closer to each other and the Co(II) complex is less stable on a clay surface than in solution.

In reality, this clay system does not work unless a different organization of the colloidal suspension is obtained. Nijs *et al.* (1982) heated a RuO_2 -hectorite mechanical mixture to collapse the interlayer space of the clay. The photosensitizer and the sacrificial reagent were then adsorbed on the external surface only. When this material was placed in suspension and irradiated with visible light, oxygen was produced until the Co(III) complex was consumed. When the reagents were mostly on the external surface and in contact with the colloidal RuO_2 , the catalyst was efficient. In contrast, the reagents in the interlayer regions could not react at the RuO_2 surfaces. This observation emphasizes again the importance of tactoid formation in restricting the availability of a catalyst in electron-transfer processes. Distributing the reagents on the external surface only, thereby making the RuO_2 catalyst fully efficient, illustrates favorable supramolecular organization.

In conclusion, when designing clays and other colloids for use in multifunctional catalytic systems, such

as those which would mimic natural processes, the notion of supramolecular organization is of primary importance.

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