REVIEW OF THE DIFFUSION OF WATER AND PYRIDINE IN THE INTERLAYER SPACE OF MONTMORILLONITE: RELEVANCE TO KINETICS OF CATALYTIC REACTIONS IN CLAYS

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Abstract—With the current interest in the use of transition metal-exchanged phyllosilicates as catalysts for novel organic syntheses, investigations into the factors which affect the movement of reactant, product, and solvent molecules into and out of their interlamellar region are of considerable importance. Mixed organic-water intercalates of a Wyoming montmorillonite, exemplified by the Na-montmorillonite-pyridine-water system which can form four different intercalates exhibiting basal spacing of 29.3, 23.3, 19.4, and 14.8 Å depending on the pyridine : water ratio, have been used as a model system. X-ray and neutron diffraction and quasielastic neutron scattering data relating to the interconversion of interlayer species indicate that access to and exit from the interlayer space is hindered at high partial pressures of water by a water-film diffusion barrier in the interparticulate voids which exist between the aggregated silicate layers. At lower water vapor pressures the rate-limiting step for interconversion from one intercalate to another is the rate of transport of reagents and products into and from the clay particles. Under conditions where these rates are fixed, the rate-limiting step is the rate of diffusion of the pyridine molecule in the lower-spacing intercalate. Processes which involve a change in basal spacing do not necessarily proceed via a single discrete step, but are also affected by the amount of water made available to the system. In organic reactions catalyzed in the interlamellar space of various cation-exchanged montmorillonites (e.g., the conversion of alk-1-enes to di-2,2′-alkyl ethers and the reaction of alcohols to form ethers), rate-determining steps similar to those found above are likely to be operative. In particular, for reactions carried out in the liquid phase, where mass transport is facile and where phase-transfer problems are avoided, such reactions are likely to be diffusion controlled.

Key Words—Catalysis, Diffusion, Interlayer space, Kinetics, Montmorillonite, Pyridine, Water.

INTRODUCTION

Montmorillonite clays or, more commonly, acid-treated montmorillonites have been used as catalysts in a wide variety of reactions over the past fifty years. Typical examples are the alkylation of phenols (Kaplan, 1966) and the dimerization and polymerization of unsaturated hydrocarbons (Hojabri, 1971). Acid treatment of the clays, however, results in a breakdown of the layer structure so that, in effect, they are high-surface area, quasi-amorphous solids with many ill-defined reaction sites. It is only recently that montmorillonites which have been only mildly treated (by cation exchange) have been investigated for the selective conversion of organic species to the desired products.

Several workers (e.g., Adams *et al.,* 1977a, 1978a, 1978b, 1979a, 1979d, 1981, 1982a, 1982b, 1983; Ballantine *et al.,* 1981a, 1981b; Bylina *et al.,* 1980) reported novel organic syntheses in the interlayer space of some trivalent metal-exchanged montmorillonites. The catalytic nature of these materials was attributed to an acidic proton resulting from the polarization of solvent water molecules by the exchangeable cations. These cations were also reported to polarize alkene double bonds and facilitate the addition of alcohols to form ethers.

Adams *et al.* (1981, 1982b) recently produced methyltertiarybutyl ether (MTBE) and isopropyltertiarybutyl ether (iPr-TBE) (effective gasoline additives for the improvement of antiknock and antismog prop-

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erties) using trivalent cation-exchanged montmorillon-ites as catalysts. It appeared that under the mild con-ditions employed (60°–90°C) a necessary condition for the formation of t-butyl ether was that one of the reac-tants could form a stable tertiary or allylic carbonium ion upon protonation and, possibly, dehydration (Adams *et al.,* 1983). Different yields of product were also observed depending upon the physical size of the reactant molecules, and these authors suggested that this difference correlated well with the rate of diffusion of these molecules or inversely with the steric hin-drance which occurred during the reaction. The low temperature coefficient reported for the ether reaction suggests a reaction involving diffusion steps. The choice of solvent for such reactions is crucial because to gain access to active sites, reactant molecules must displace solvent molecules from the coordination sphere of the cations.

The overall reaction obviously depends on a number of equilibria involving the distribution of reactant mol-ecules between clay and external solution, and possible further equilibria controlling the distribution of these reactant molecules between active sites in the clay and remaining interlayer space. These equilibria are, of course, sensitive to the presence of non-reactive sol-vent molecules which modify the concentrations of participating molecules within the interlayer space and which themselves are competitors for coordination at active sites.

To date, the work reported in the literature con-cerning host/mixed guest systems has been mainly con-fined to equilibrium studies of the selective sorption of specific adsorbates from binary mixtures in the gas and vapor phase (Barrer, 1978) and solution (Theng, 1974). The quantitative consideration of the diffusion of occluded moeities (other than cations) in zeolites, layered dichalcogenides, and clay minerals appears to have been restricted to the investigation of host/single guest species. Because of their industrial importance the diffusion of gases, such as Ar, Ne, O_2, N_2, H_2, and cyclic, aromatic, and aliphatic hydrocarbons, through zeolites has been well documented (see, e.g., Barrer, 1978; Kärger and Caro, 1977; Yucel and Ruthven, 1980a, 1980b; Bülow *et al.,* 1980).

The examples of clay catalysis outlined above, how-ever, clearly illustrate that information derived from single host/guest studies inadequately describe such a complex system and that the study of diffusion in clay intercalates containing mixtures of reactant and prod-uct species is important in the determination of reac-tion pathways, particularly in the identification of any rate determining process. The Na-montmorillonite-pyridine-water system, with its wealth of intercalated forms that are easily converted to one another, lends itself as a model system for studying the factors af-fecting the diffusion of species into and out of the in-terlayer region of clays. For this model system the rate of conversion of a high spacing (HS) intercalate to one of lower spacing (LS) depends upon several factors: (1) movement of water molecules to the edge of the clay particle, a process that depends upon the partial pres-sure of water and flow rate of any carrier gas; (2) dif-fusion of water through the interface at the edge of the clay particle; (3) diffusion of water through the HS phase; (4) diffusion of pyridine through the HS phase; (5) diffusion of water through the LS phase; (6) diffusion of pyridine through the LS phase; (7) diffusion of pyr-idine through the interface at the edge of the clay par-ticle; and (8) loss of pyridine to the atmosphere, which is dependent upon the flow rate of any carrier gas.

It is the purpose of the present work to review the results of several studies concerned with the interde-pendent roles of the diffusion of water and pyridine in the mixed Na-montmorillonite-pyridine-water system and to compare them (1) directly with the results for the diffusion of water in clay-water systems, and (2) in general terms with the factors influencing the diffusion or organic moeities in the channel network of zeolites. In addition, the results obtained for the title system will be applied to those reported on clay/organic re-actions, such as the formation of ethers (Adams *et al.,* 1981, 1982b).

EXPERIMENTAL

Neutron methods

Neutron diffraction and quasielastic neutron scat-tering have, in recent years, been utilized to investigate the diffusion characteristics of single guest species, such as ammonia and pyridine, in tantalum disulphide (Riekel and Schöllhorn, 1976; Riekel, 1978; Riekel and Fischer, 1979; Riekel *et al.,* 1979) and water in various cation-exchanged phyllosilicates (Ross and Hall, 1980; Cebula *et al.,* 1981). The use of neutron scattering tech-niques for the determination of diffusion coefficients is greatly facilitated by the very dissimilar incoherent scattering cross-sections for hydrogen and deuterium (79.7×10^{28} m^2 and 2.0×10^{28} m^2, respectively). This dissimilarity results in neutrons being extremely sen-sitive to hydrogen-containing materials. Deuteration of hydrogenous compounds markedly reduces the in-coherent scattering enabling isotopic exchange to be followed by neutron diffraction under favorable con-ditions. In contrast, incoherent quasielastic neutron scattering (QENS) utilizes the large incoherent cross-section of hydrogen to identify translations which in-corporate hydrogen atom transport.

Materials and methods

The montmorillonite used was the <2-μm fraction of a sample of Wyoming bentonite supplied by Volclay Ltd., Wallasey, Cheshire. The fully Na-exchanged form
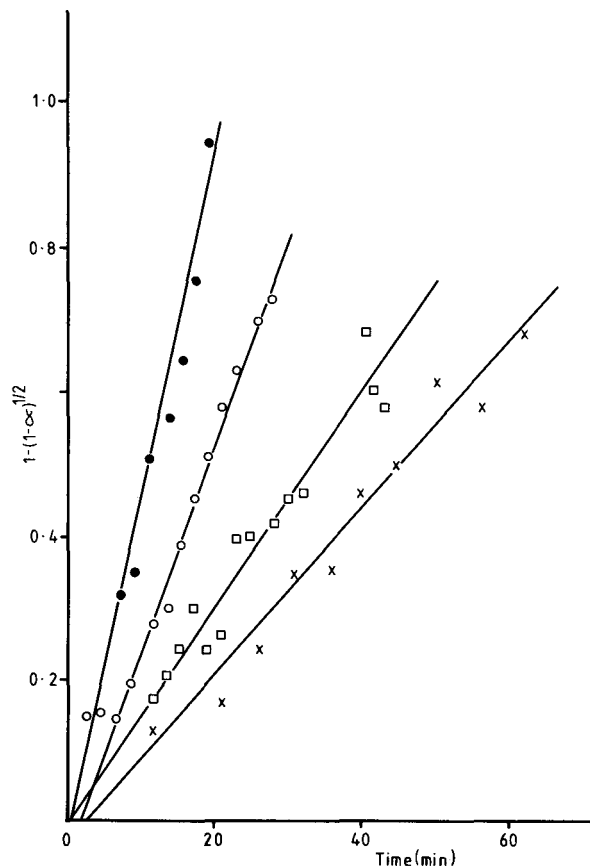
Figure 1. Illustration of fit of experimental data to contracting circle formulation. Increase in intensity of the 001 peak of the 23.3-Å form of the Na-montmorillonite/pyridine/water system when subjected to a flow rate for He/D$_2$O of 20 cm^3/sec. ($\times$ = 25°C, 24 mm Hg; $\square$ = 35°C, 42 mm Hg; $\bigcirc$ = 45°C, 72 mm Hg; $\bullet$ = 55°C, 118 mm Hg.)

was prepared by immersing the clay in a 0.3 M solution of NaCl for 24 hr followed by successive centrifugation and washing steps until the sample was free of excess exchanging salt. Chemical analysis by standard literature procedures (Bennet and Reed, 1971) gave 53.7% SiO$_2$, 17.6% Al$_2$O$_3$, 2.5% MgO, 2.6% Fe$_2$O$_3$, and 0.9% F, which is consistent with a layer formula of (Al$_{2.8}$Mg$_{0.5}$Fe$_{0.3}$)Si$_8$O$_{20}$(OH)$_4$. The cation-exchange capacity of the air-dry material, as determined by a flame photometric method (Adams et al., 1977b) was 66 ± 2 meq/100 g of clay. Thin flakes (~6 × 1 × 0.05 cm^3) for neutron studies were prepared by evaporating an aqueous slurry on a polyethylene backing which was subsequently removed. For the X-ray diffraction studies samples were prepared by evaporating a saturated clay suspension on glass slides to produce oriented films of dimensions ~2.5 × 1.3 × 0.025 cm^3.

The details of the experimental conditions are reported elsewhere: X-ray powder diffraction studies (XRD) by Adams and Breen (1982); neutron diffrac-

tion (ND) by Adams et al. (1979b, 1980, 1983); and quasielastic neutron scattering (QENS) by Adams et al. (1979c). A summary of the essential conditions is given in Table 1. The ND and QENS studies were carried out at the Institut Laue-Langevin in Grenoble, France.
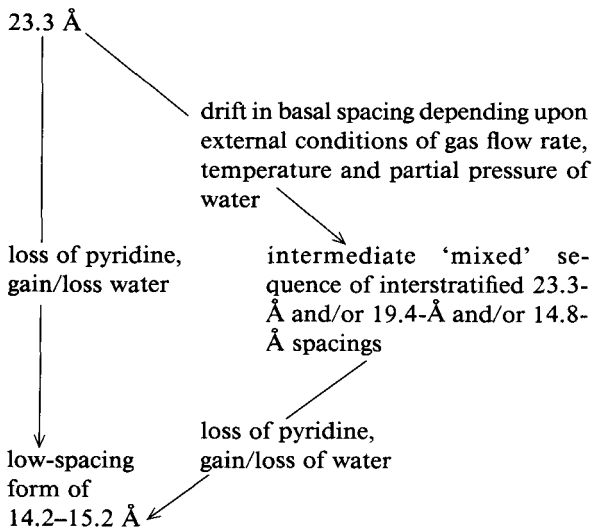
Treatment of kinetic data

The rate coefficients for the conversions between intercalates having different basal spacing were derived from the diffraction studies and were calculated by treating the data according to a contracting circle kinetic formulation, $kt = 1 - (1 - \alpha)^{1/2}$ (Garner, 1955) where α is the reaction fraction complete. The derivation of this formula assumes that the particles under consideration are circular, of equal size, and that there is instantaneous nucleation on the particle surface at the beginning of the reaction followed by an inward movement of an interface between reactant and product form. If the lamellar nature of the clay sample is considered, this model is acceptable, and the fit of the experimental data to the contracting circle equation is quite good, as illustrated in Figure 1.

SUMMARY OF PREVIOUS RESULTS

Intercalate interconversions (reactions)

Van Olphen and Deeds (1961) showed that the Na-montmorillonite-pyridine-water system can have different basal spacings of 29.3, 23.3, 19.4, and 14.8 Å depending upon the pyridine/water ratio. Figure 2 shows tentative structures for the four different intercalates. Each intercalate has been shown to be stable under a particular set of conditions of water vapor pressure, temperature, pyridine content of clay, etc. (Van Olphen and Deeds, 1961; Adams and Breen, 1982), and interconversion between phases occurs therefore with loss of either pyridine or water and the gain of either water or pyridine as in:

23.3 Å

drift in basal spacing depending upon external conditions of gas flow rate, temperature and partial pressure of water

loss of pyridine, gain/loss water

intermediate 'mixed' sequence of interstratified 23.3-Å and/or 19.4-Å and/or 14.8-Å spacings

low-spacing form of 14.2–15.2 Å

loss of pyridine, gain/loss of water

The variation in d-spacing quoted for the LS form does not represent an uncertainty but indicates the range of basal spacings resulting from slight differences in water content (Adams and Breen, 1982).

Due to the complexity of the interconversion processes between the different forms of the system under discussion it was necessary to establish the mechanism by which the conversion took place before the rate at which it occurred could be determined. Adams and Breen (1982) showed that the route taken for a particular interconversion between intercalates depends upon the external conditions to which the intercalate is subjected. The mechanism of conversion was examined by following the intensity and position of the 001 peak as a function of time using XRD, as shown for the 23.3-Å form in Figure 3. During the conversion of the $\geq$19.4-Å intercalates to the 14.2–15.2-Å form, the position of the 001 peak of the HS form drifted to a stable value which can be correlated with a regular interstratification having the basal spacings listed in Table 2.

Figure 4 summarizes schematically the similarity of the mechanisms of conversion for the three HS (29.3-Å, 23.3-Å, and 19.4-Å) intercalates to the lower spacing form. It is apparent that the process is not simple. Figure 4a, in which the intermediate sequence contains no 23.3-Å layers, represents the moisture-free limit of the conditions studied by Adams and Breen (1982). When more water is available to the system, a 23.3-Å layer is maintained in the interstratified complex (cf. the intermediate sequences formed by the HS forms at 22°C and 28°C in Figures 4b, 4c, and 4d with that in Figure 4a). During this set of experiments the amount of water available to the 23.3-Å intercalate was always
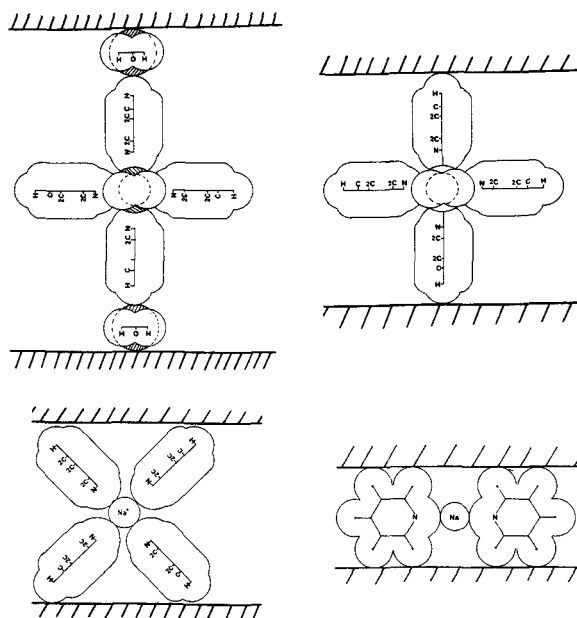

Figure 2. Four different forms of the Na-montmorillonite/pyridine/water system viewed in the *bc* plane. (a) 29.3 Å; (b) 23.3 Å; (c) 19.4 Å; (d) 14.8 Å.

insufficient to maintain the spacing of all the layers at 23.3 Å (Figure 4b). Adams *et al.* (1983) showed that it is necessary to use the high external vapor pressures provided by flow rates of the D_2O-saturated carrier gas of 7 cm³/sec and 20 cm/sec to maintain a repeat spacing of 23.3 Å.

The (19.4 Å + 14.8 Å) intermediate sequence formed

Table 1. Summary of the experimental and instrumental conditions utilized.

Technique	Sample preparation	Instrument utilized	Instrumental conditions	Experimental conditions		
				Temperature (°C)	Flow rate (cm³/sec)	Partial pressure of water (mm Hg)
X-ray diffraction	a	Philips PW 1050 diffractometer	$\lambda = 1.5418$ Å 40kV; 36 mA 2° 2θ/min	22 28 37	0.9, 2.7, 6.0 0.9, 2.7, 6.0 0.9, 2.7, 6.0	6.7, 16.3, 21.3 9.3, 22.5, 29.4 13.8, 33.5, 43.8
Neutron diffraction	b	D1B (f)	$\lambda = 2.55$ Å	25 35 45 55	0.6, 7, 20 7, 20 7, 20 7, 20	24 42 72 118
Neutron diffraction	c	D16 (f)	$\lambda = 4.16$ Å	38–45	—	—
Quasielastic neutron scattering	d, e	IN1O (f)	$\lambda = 6.284$ Å	23.5 26 42	—	—

a = immersion in reagent grade pyridine, gross surface excess wiped off with tissue; subjected to a controlled flow of N_2/H_2O.
b = as 'a' but using He/D_2O gas flow and deuteropyridine (99% of the atoms replaced by deuterium) rather than pyridine.
c = immersion in reagent grade pyridine, gross surface excess wiped off with tissue, exposed to 99 atom % d C_5D_5N.
d = interlayer H_2O replaced by D_2O followed by immersion in reagent grade pyridine, gross surface excess wiped off with tissue.
e = immersed in 99 atom % d C_5D_5N, gross surface excess wiped off with tissue.
f = details of these instruments are given; in Neutron Beam Facilities at the HFR Available for Users (1977).

Table 2. Final peak positions of the 001 peak of the 23.3-Å form and the proposed intermediate sequence that they represent.

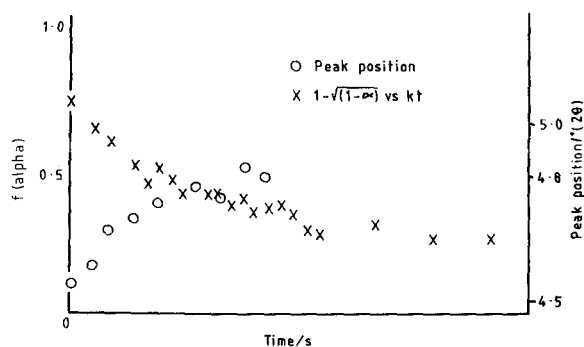| Final peak position (°2θ)	Suggested indexing of peak
3.79	001 of 23.3 Å
4.0	003 of (23.3 Å + 23.3 Å + 19.4 Å)
4.15	002 of (23.3 Å + 19.4 Å)
4.27	003 of (23.3 Å + 19.4 Å + 19.4 Å)
4.31	003 of (23.3 Å + 23.3 Å + 14.8 Å)
4.61	003 of (23.3 Å + 19.4 Å + 14.8 Å)
4.95	003 of (19.4 Å + 19.4 Å + 14.8 Å)
5.1	002 of (19.4 Å + 14.8 Å)

Figure 3. Plot of decrease in intensity of the 001 peak of the 23.3-Å form of the Na-montmorillonite/pyridine/water system (at 23°C, partial pressure of water of 6.7 mm Hg, and a flow rate for N_2 carrier gas of 0.9 cm^3/sec) as contracting circle kinetics. Figure illustrates the correlation between the termination of the early rapid decrease of the rate curve and the stabilization of the peak position.

at zero partial pressures of water shows that if only a small amount of water is available to the sample, some or all of the 23.3-Å intercalate collapsed to the 19.4-Å form en route to the 14.8-Å form. Despite this indication of different mechanisms the rate constants for the increase in intensity of the 001 XRD peak of the 14.8-Å form generally increased with flow rate at a given temperature and partial pressure of water. Under certain conditions, however, the decrease in intensity of the 001 peak of the 23.3-Å form was retarded by the highest partial pressures of water employed.[1] This was interpreted by Adams and Breen (1982) to be due to a build up of interparticulate and surface water which acts as a barrier to the diffusion of pyridine and/or water out of the layers with a 23.3-Å spacing.

The existence of such a surface-film diffusion barrier was corroborated by the ND studies of Adams *et al.* (1983). At 25°C and at flow rates for He/D_2O of 7 cm^3/sec and 20 cm^3/sec, the combination of low temperature, high flow rate, and physical size of the samples (~6 × 1 × 1 cm^3) resulted in the prevention of the collapse of the 23.3-Å intercalate to the 14.8-Å form by severely restricting the diffusion of pyridine out of the interlayer space. The large amount of D_2O available under these conditions resulted in further adsorption of water molecules causing a stepwise increase in basal spacing to 29.4 Å. At or above 35°C the 29.4-Å form was not observed. This behavior is illustrated in Figure 5, where the diffraction profiles observed under different experimental conditions are summarized. The increased effect of the diffusion barrier at a flow rate for He/D_2O of 20 cm^3/sec was evident in the extra ~17 kJ/mole in the activation energy for water diffusion compared with that for a flow rate of 7 cm^3/sec.

Overall, it appears that when no surface film barrier

of water is present, the rate of transformation between intercalates is dependent upon the transport of reagents to and from the clay particles.

Diffusion of interlayer species

On the timescale of a QENS experiment a diffusing molecule in these systems experiences only one type of environment. Consequently, the diffusion coefficients derived from this method are unaffected by external diffusion barriers and yield interlayer diffusion coefficients directly. Cebula *et al.* (1981) and Ross and Hall (1980) reported QENS results for water diffusion in the one-, two-, and three-layer hydrates of various cation-exchanged montmorillonites. Their results show that the diffusion process is simultaneous rotation and translation characterized by translational diffusion coefficients of 3–10 × 10^{-10} m^2/sec, the magnitude of which depends on the water content of the clay. Adams *et al.* (1979c) conducted a similar investigation on the 23.3-Å form of the Na-montmorillonite/pyridine/water system and showed that the interlamellar water has a translational diffusion coefficient of ~6 × 10^{-11} m^2/sec, which is considerably less than the 10^{-9} m^2/sec found for water in clays with 18-Å basal spacings (Cebula *et al.*, 1981). A parallel investigation by Adams *et al.* (1980) showed that the interlayer pyridine in the same 23.3-Å complex was moving at a rate of <10^{-12} m^2/sec. Obviously the immobile pyridine in the 23.3-Å mixed pyridine-water intercalate markedly affects the diffusion of the interlamellar water.

ND studies on the 23.3-Å form of the Na-montmorillonite-pyridine-water system (Adams *et al.*, 1979a; Adams and Breen, 1983) revealed that the structure factor changed when the interlayer H_2O was replaced by D_2O. This enabled the determination of the macroscopic diffusion coefficients by following the

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[1] Unfortunately, the rate constants for the corresponding decrease in intensity of the 001 peak of the 23.3-Å form cannot be explained unambiguously because of the several different intermediate complexes which are formed.

increase in intensity of the 001 peak of the 23.3-Å form as a function of time. Adams *et al.* 1979a) and Adams *et al.* (1983) showed that exchange of D_2O for H_2O in the interlayer space of the 23.3-Å form was characterized by a macroscopic diffusion coefficient of $\sim 10^{-16}$ m^2/sec at flow rates for He/D_2O of 7 and 20 cm^3/sec with corresponding activation energies of 21 and 38 kJ/mole. Identical experiments conducted on the exchange of C_5D_5N for C_5H_5N (Adams *et al.,* 1980) in the 23.3-Å intercalate yielded diffusion coefficients of the same order of magnitude as that for water but with an activation energy of 129 kJ/mole.

The vastly different values derived from QENS and ND results can be explained by the timescale of the two experiments. The QENS results afford a measure of the "instantaneous" diffusion rate in the interlamellar space, whereas the ND results reflect that the diffusing species encounters a range of different environments over a period of time. Although no data concerning the diffusion of pyridine or water in the 14.8-Å form are available, consideration of the molecular size and ligand–cation bond strengths suggests that diffusion of pyridine must be rate determining in this low-spacing form. Physically, this relation is realistic because, as Figure 6 shows, the water molecules diffuse from the edge to the center of the sheets so that a 'sandwich' is formed with a large central but small peripheral spacing. Consequently, most of the pyridine has to diffuse through the 14.8-Å form to leave the interlayer region.

DISCUSSION

Comparison of diffusion in clays and zeolites

The paucity of available data pertaining to the factors which influence diffusion in phyllosilicates necessitates an unsatisfactory comparison with data obtained for related systems within the intrinsically similar but structurally different framework of zeolites. At first glance, the framework structure of a zeolite may seem far removed from that of the layer structure of clays; however, consideration of Figure 6 shows that the small peripheral spacing of the clay layers mimics the size of the zeolitic windows. It is through such a barrier that counterdiffusing reactant and product molecules must proceed for reaction to continue.

Diffusion within the zeolite structure is influenced by several factors including the geometry and dimensions of the channel network; the size, charge, and
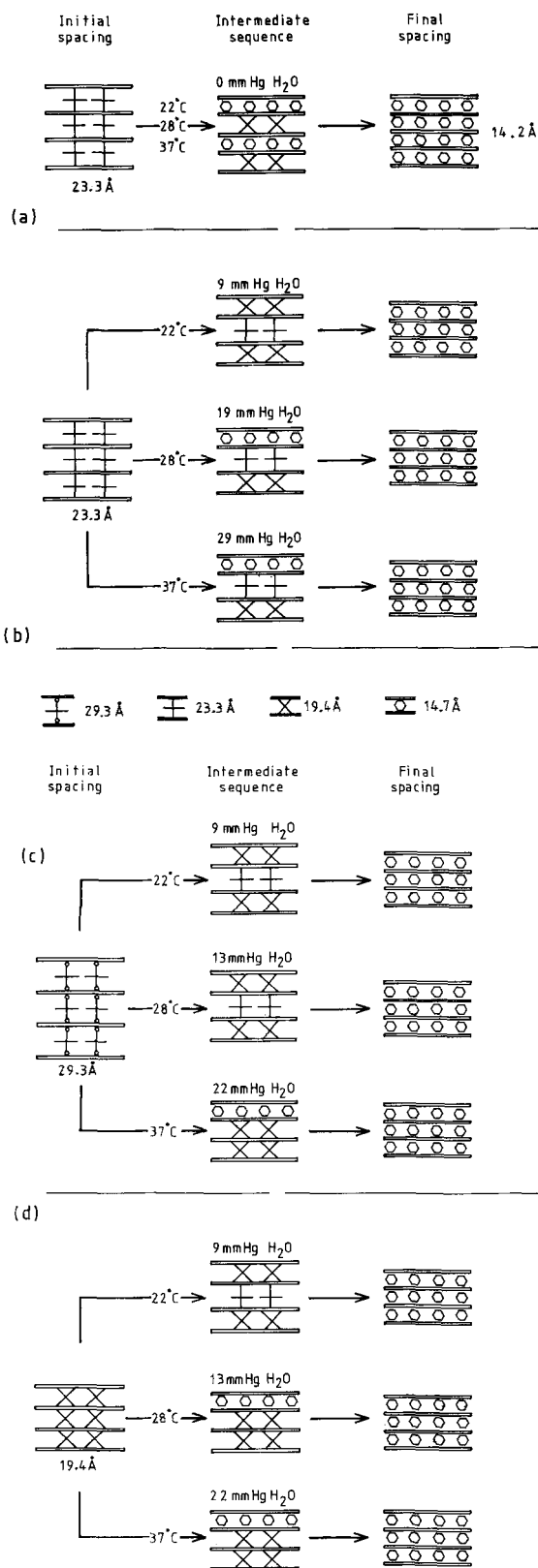
$\longrightarrow$

Figure 4. Schematic summary of the temperature and partial pressure of water dependence of the conversion of the ≥ 19.4-Å intercalates of the Na-montmorillonite/pyridine/water system to the lower spacing 14.7–15.2-Å form.
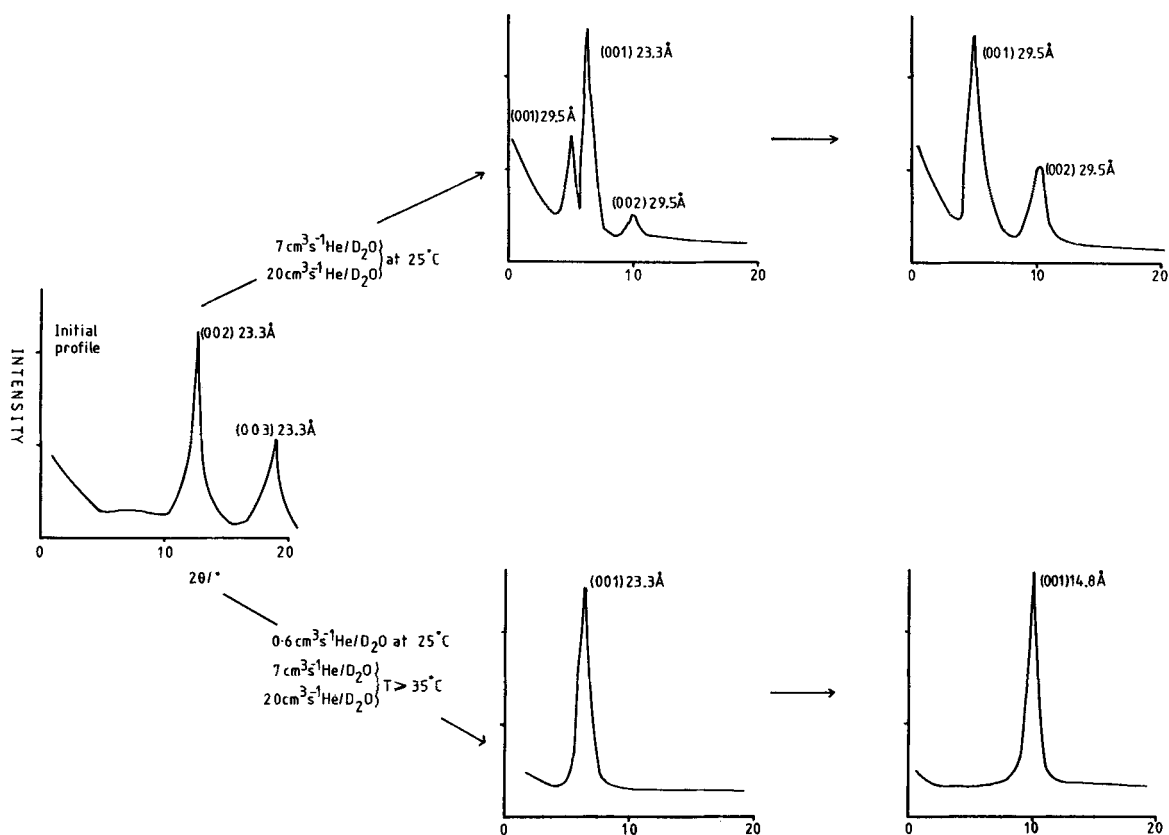
Figure 5. Schematic representation of the diffraction profiles displayed by samples exposed to differing amounts of D₂O vapor at several temperatures and flow rates of the carrier gas.

concentration of cations; the size, shape, polarity, and flexibility of penetrant molecules; and the presence of impurity molecules (Barrer, 1978). In addition to these factors Moore and Katzer (1972) showed that counterdiffusion of products out of zeolite catalysts may seriously affect the apparent activity and selectivity for a specific reaction because intermolecular interactions between the counterdiffusing reactant and product molecules contribute to a reduction in the rates of diffusion. Obviously, the situation with respect to diffusion in phyllosilicates is influenced to a greater or lesser extent by all of these factors. Little is known concerning the effect of molecular size and shape of penetrant molecule on the rate of diffusion, but the type of cation and polarity of the occluded molecule certainly exerts an influence. Preliminary investigations in these laboratories indicate that benzonitrile is held more strongly than pyridine in montmorillonite exchanged with Na, Li, and Sr and that benzonitrile and pyridine are both held more strongly in the sequence Sr > Li > Na. In contrast to the permanent size and shape of the channels in an outgassed zeolite, the geometry and dimensions of the 'channel network' in the interlayer space of clay minerals are not fixed but are governed

by the size of the adsorbed molecules and the distance between adjacent interlayer cations. This situation makes it extremely difficult to predict the diffusional characteristics, particularly in clay/organic systems where counterdiffusion of molecules of dissimilar size is involved.

The open structure of an outgassed zeolite allows the rapid uptake of most organic molecules with diameters ≤ 8 Å, and the diffusion coefficients follow the trend alkanes > alkenes > polar compounds. The increased affinity of polar sorbates for the zeolite results in longer residence times at each site and therefore slower transport rates. Consequently, the presence of preadsorbed 'impurity' molecules in zeolites can reduce diffusion coefficients by a factor of 10^3 to 10^4 by forming periodic potential energy barriers in the narrow channels of the zeolites, the height of which varies according to the relative dimensions of channel and molecule (Barrer and Robbins, 1953; Barrer and Rees, 1954). In clay catalysis, however, the presence of a small number of preadsorbed molecules is essential because the Bronsted acidity which gives rise to the catalytic activity results from the polarization of solvent water molecules by the interlayer cations. In contrast to the sit-

uation in zeolites, a small number of preadsorbed water molecules are likely to accelerate the initial rate of ingress of certain penetrant molecules by propping the layers apart and consequently reducing the energy barrier associated with separation of the completely collapsed layers of an outgassed clay. Moreover, it is unlikely that the potential minimum associated with a cation-alkane interaction would provide sufficient impetus for the rapid adsorption of alkane molecules as exhibited by zeolites.

More recently the existence of surface barriers and their effect on the diffusion of aliphatic, cyclic, and aromatic hydrocarbons in zeolite crystals at low sorbate concentrations has been the subject of some controversy (Kärger and Caro, 1977; Yucel and Ruthven, 1980a, 1980b). A comprehensive investigation by Bülow et al. (1980), in which both the NMR-pulsed field-gradient technique and the more conventional mass-uptake kinetics approach were applied to molecules adsorbed in zeolites, resulted in the consideration that such a barrier does indeed exist if the radius of the zeolite crystals is between 0.7 and 13 μm, a particle size range which encompasses that of the montmorillonite used in this study. The presence of water-film diffusion barriers have been postulated by Weber and Roy (1965) and Brindley et al. (1967) to explain the retardation of the dehydration of clay minerals at high partial pressures of water. The retardation of the conversion of the HS to LS intercalates of the title system and the promotion of further adsorption of water molecules into the 23.3-Å form in the ND studies are irrefutable evidence for a water-film diffusion barrier.

Possible diffusion-controlled, clay-catalyzed reactions

The preceding comparison clearly demonstrates that further information concerning the diffusion of organic molecules in clay minerals is required before rate-controlling steps in some clay-catalyzed reactions can be unambiguously attributed to mass-transport effects. Nevertheless, in the present context it is advantageous to consider those examples of clay catalysis in which the rate-determining step may be diffusive in nature. Adams et al. (1982a) conducted a detailed study of the formation of di-2,2'-hexylether from hex-1-ene over a Cu^{2+}-exchanged montmorillonite at <100°C. The active site appeared to be an acidic proton produced by the polarization of a water molecule in the primary coordination sphere of Cu^{2+}. The addition of water across the double bond at the active site resulted in the formation of hexan-2-ol which was held in the coordination sphere of the copper ion until another alkene molecule diffused to this site and formed the dihexylether. The analysis of the supernatant reaction mixture and that extracted from the interlamellar space showed an unequal distribution of products between the supernatant liquor and the interlayer region. Very
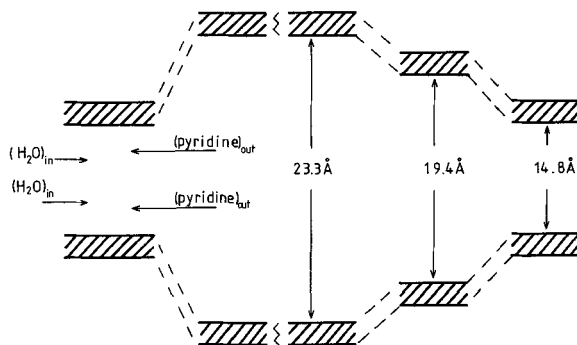

Figure 6. Possible mechanisms of collapse for the 23.3-Å form of the Na-montmorillonite/pyridine/water system to the lower spacing form. (1) Conversion directly to the 14.8-Å form on the left and (2) Conversion to the 14.8-Å form via the 19.4-Å form on the right.

little product ether remained in the clay, but a much higher concentration of hexan-2-ol was noted in the clay than in solution. Adams et al. (1982a) attributed these results to the rapid diffusion of the ether molecules out of the interlamellar space. Moreover, when the Cu^{2+}-clay was immersed in hex-1-ene, it took several days for the basal spacing to reach a maximum, indicating that diffusion of hex-1-ene into the Cu^{2+}-montmorillonite to form the initial clay/hexene complex was very slow. Consequently it is possible to envisage a process in which the rate-determining step is the diffusion of the essentially hydrophobic hex-1-ene into the hydrous clay, after which the hexan-2-ol and subsequently the outward-diffusing dihexylether holds the layers apart to permit more facile diffusion of hex-1-ene to the active site, provided the interaction between hex-1-ene and di-2,2'-hexylether does not present too high a potential barrier to diffusion. This suggestion fits well with the measured pseudocatalytic rate of reaction (Adams et al., 1982a).

Adams et al. (1981) studied the low-temperature (<60°C) reaction of alcohols to form t-butylethers utilizing montmorillonite exchanged with Fe^{3+}. The low-temperature coefficient of the ether reaction indicated that the reaction was diffusion controlled. In the reaction of tertiary butanol (t-BuOH) with methanol (MeOH), n-propanol (n-PrOH), or isopropanol (i-PrOH) equilibrium was rapidly attained, although the position of the equilibrium depended upon the particular alcohol used in conjunction with t-BuOH in the order MeOH > PrOH > i-PrOH. This sequence correlates well with the expected rate of diffusion of these alcohols into the interlamellar space, and equally so with that of the product ether out of the interlayer region.

CONCLUSIONS

It is apparent from the above work on our model system that a range of different intercalates can be

formed depending upon the exact stoichiometric relationship between guest species in the interlayer space of a montmorillonite clay. The interconversions between intercalates that we have studied are simple models for processes which occur during a reaction catalyzed by a cation-exchanged montmorillonite. The mechanisms of the interconversions are complex; regular interstratified materials are the intermediates, and these depend intimately upon the chemical environment and temperature. At high water contents, the rate of "reaction" depends upon diffusion though an interparticulate water film barrier, whereas at lower water content the rate-determining step appears to be transport of reagents and products to and from the clay particles. In the absence of a water-film diffusion barrier the diffusion of the bulky organic species through the lower spacing intercalate is considered to be the slowest diffusion step.

The work concerning diffusion in clay systems reported and discussed here has all been conducted at high sorbate concentrations which is exactly the situation pertaining in the recent investigations into catalysis of organic reactions by clay minerals. Further information concerning the influence of molecular size, shape, polarity, and flexiblity on the rate of diffusion, however, is required before a full understanding of the role of mass-transfer effects in clay-catalyzed reactions can be acquired.

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