

THE INFLUENCE OF HEAT-STABLE INTERCALATE ON THE RATE OF DEHYDROXYLATION OF SMECTITE¹

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Abstract—The rates of dehydroxylation of smectites intercalated with the decomposition products of $\text{Ni}(\text{phen})_3\text{SO}_4$ are from 2 to 4 times greater than those of clays without the heat-stable intercalate. These results suggest that the intercalated material, in keeping the clay sheets separated, provides a more ready avenue for water loss during the dehydroxylation process.

Key Words—Activation energy, Dehydroxylation, Intercalate, Reaction rate constant, Smectite.

INTRODUCTION

The temperature of dehydroxylation of smectite has been shown to be affected by a variety of factors, among which are the chemical composition of the layer structure and the kind of exchange cation on the surface (Mackenzie, 1970). The reaction kinetics for the dehydroxylation of clays has been suggested to be controlled by water diffusion (Achar *et al.*, 1966).

Loeppert *et al.* (1979) produced heat-stable expanded smectite and vermiculite by saturating the exchange sites with complex cations of o-phenanthroline or bipyridyl plus intercalation of some excess sulfate salt of the complex cation, followed by firing to temperatures as high as 550°C. Such materials can have significant internal surface area. Since the kinetics of dehydroxylation has been suggested to be diffusion controlled, the presence of an intercalate might provide avenues for the more rapid loss of water resulting from the dehydroxylation reaction than would be the case where the smectite layers are firmly collapsed upon one another as a result of dehydration. Barnhisel and Rich (1963) observed that dehydroxylation of smectite began at a lower temperature when an intercalate of $\text{Al}(\text{OH})_3$ was present. The objective of the present work was to compare the rates of dehydroxylation of smectites with and without the presence of an intercalated material.

EXPERIMENTAL

Preparation of clays and clay complexes

Montmorillonite (Upton, Wyoming, API standard 25) and nontronite (Garfield, Washington, API standard 33A) were saturated with Na^+ and the $<2\text{-}\mu\text{m}$ fractions obtained. Portions of the clays were then saturated with Ni^{2+} by ion exchange with the chloride salt. $\text{Ni}(\text{phen})_3\text{SO}_4$ -clay complexes were prepared by sus-

pending 200 mg of Na^+ -saturated freeze-dried clay in 50 ml of deionized water and then adding 50 ml of water containing 2.0 cation-exchange capacity (CEC) equivalents of $\text{Ni}(\text{phen})_3\text{SO}_4$. The suspensions were allowed to stand for 24 hr. Self-supporting films of Ni^{2+} -clays and $\text{Ni}(\text{phen})_3\text{SO}_4$ -clays were prepared by pipetting clay suspensions into aluminum dishes and evaporating the water to give films containing approximately 0.5 mg of clay per cm^2 .

Isothermal dehydroxylation studies

Isothermal dehydroxylation studies were performed on self-supporting films which were placed securely in Al-foil holders. Holders were designed so that identical portions of the film could be removed and replaced with respect to the infrared beam. Samples were placed in a muffle furnace (controlled to $\pm 1^\circ\text{C}$) which had previously been equilibrated to the desired temperature and were heated for the desired time interval. Upon removal from the furnace, films were placed on a stainless steel surface to facilitate rapid cooling, thus quenching the reaction. Infrared (IR) spectra were obtained with a Beckman IR-7 instrument. Spectra were recorded in the absorbance mode, and the intensity of the octahedral-OH stretching band (montmorillonite, 3635 cm^{-1} ; nontronite, 3564 cm^{-1}) was used as a measure of relative concentration of octahedral-OH groups. Clay films heated to the temperatures used in the isothermal studies showed no appreciable evidence of rehydration as would be indicated by changes in the OH-stretching band upon removal from the furnace and exposure to the atmosphere; therefore, no special handling was required.

In these studies it was assumed that the samples came rapidly (a few seconds) to temperature when placed in the furnace and, conversely, cooled rapidly when removed from the furnace, thus quenching the dehydroxylation reaction. The use of very thin films (0.5 mg/cm^2) and thin aluminum foil holders fulfilled the requirements of rapid heat transfer.

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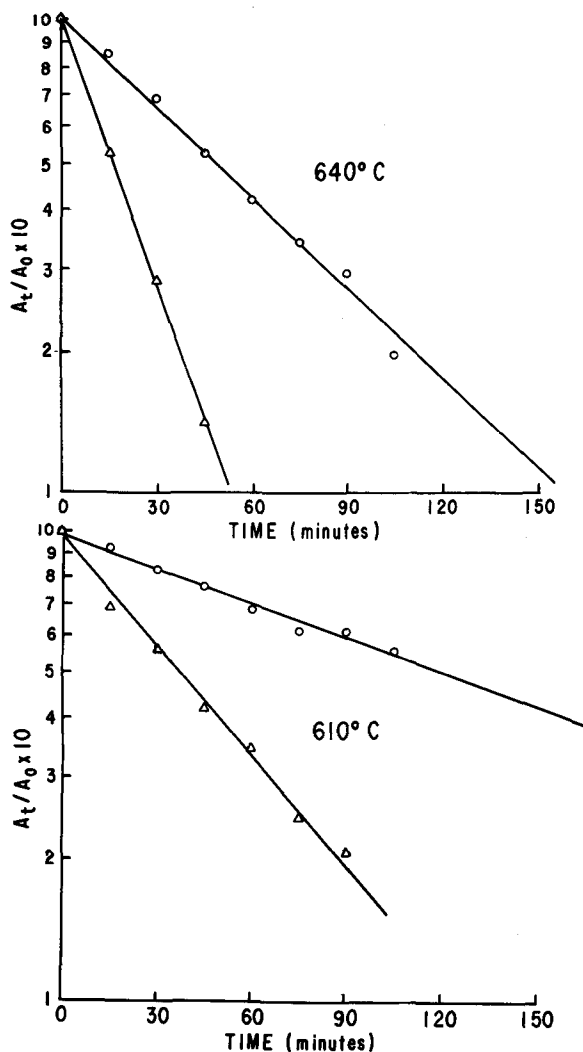


Figure 1. First order plots at two temperatures for the dehydroxylation of Upton smectite with (triangles) and without (circles) a heat-stable intercalate. A_t is the absorbance at time t , and A_0 is the absorbance at time zero.

RESULTS

The change in absorbance of the hydroxyl stretching vibrations of Ni^{2+} -montmorillonite and -nontronite and of $\text{Ni}(\text{phen})_3^{2+}$ -montmorillonite and -nontronite with time near temperatures of dehydroxylation, are shown in Figures 1 and 2. A_0 represents the absorbance of the OH-stretching vibration at the start, while A_t represents the absorbance at time t . Plots of these data according to the mathematics of first order kinetics were made to present the data and do not necessarily represent the kinetics of the dehydroxylation reaction itself. The crucial effect of the presence of an interlayer material [$\text{Ni}(\text{phen})_3^{2+}$ and its decomposition products] in significantly accelerating dehydroxylation,

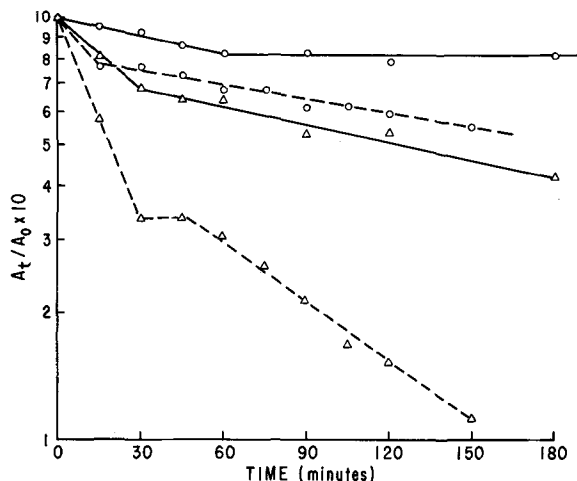


Figure 2. First order plots for the dehydroxylation of nontronite with (triangles) and without (circles) a heat-stable intercalate at 370°C (solid lines) and 400°C (dashed lines). A_t and A_0 are the absorbances at times t and zero, respectively.

is obvious for both the montmorillonite and nontronite smectites. X-ray powder diffraction patterns of $\text{Ni}(\text{phen})_3\text{SO}_4$ -montmorillonite and -nontronite complexes show that upon firing to the dehydroxylation temperature, expanded phases are maintained (Loeppert *et al.*, 1979). However, the comparable Ni^{2+} -saturated clays collapsed to approximately 9.3 Å. The following simple reaction may describe the process:



where M represents octahedral metal ions. A number of workers, e.g., Heller *et al.* (1962), have shown that there is reversibility in the dehydroxylation process of smectite so that if the concentration of water in the structure builds up from the above reaction, it will have a depressing effect on further dehydroxylation, as in the case of the Ni-smectites where the collapsed structure presents a formidable barrier to water diffusion. On the other hand, where an intercalated material prevents complete collapse of the clay sheets onto one another, an avenue is presented for the more ready diffusion of water through the relatively porous material and away from the dehydroxylation sites, thus reducing the magnitude of the reverse reaction of rehydroxylation.

An interesting contrast is the difference in the nature of the curves between the Upton smectite and the nontronite systems. The Upton smectite (Figure 1) shows uniform first order plots throughout the dehydroxylation process, while the nontronite systems (Figure 2) show a break in the slope of the plots suggesting changes in the nature of the system which affect the rate-limiting process. At this point it is not possible to give a satisfactory explanation for the change in rate of

Table 1. First order reaction rate constants and apparent activation energies for the dehydroxylation of Upton smectite and Garfield nontronite.

	Reaction rate constants (sec ⁻¹)		E _a (kilocal- ories/ mole)
	610°C	640°C	
Ni ²⁺ -smectite	1.00 × 10 ⁻⁴	2.45 × 10 ⁻⁴	48.3
Ni(phen) ₃ ²⁺ - smectite	3.08 × 10 ⁻⁴	7.28 × 10 ⁻⁴	46.2
	370°C	400°C	E _a (kilocal- ories/ mole)
Ni ²⁺ -nontronite	k ^{1*} 0.55 × 10 ⁻⁴	3.05 × 10 ⁻⁴	48.5
	k ^{11*} N.D.	0.45 × 10 ⁻⁴	—
Ni(phen) ₃ ²⁺ - nontronite	k ^{1*} 2.18 × 10 ⁻⁴	5.31 × 10 ⁻⁴	25.2
	k ^{11*} 0.55 × 10 ⁻⁴	1.66 × 10 ⁻⁴	28.6

* k¹ and k¹¹ are the rate constants for the first and second portions of the dehydroxylation curves, respectively.

dehydroxylation of the nontronite system except to suspect that the iron in the octahedral layer may be some way implicated. The iron may be involved in oxidation/reduction reactions which may have some influence on the dehydroxylation process, or perhaps the break in the curves may result from formation of another phase of iron such as an oxide (C. B. Roth, Department of Agronomy, Purdue University, West Lafayette, Indiana, personal communication) which in turn may alter the rate of dehydroxylation.

The reaction rate constants and apparent activation energies appear in Table 1. The apparent activation energies were calculated for the smectite systems using the Arrhenius equation. Whether or not these calculated activation energies represent those of chemical kinetics or of diffusion of water is, of course, open to question. If the difference in dehydroxylation rates between Ni²⁺- and Ni(phen)₃²⁺-smectites is attributed to more rapid water loss in the latter system, these values must be attributed to the activation energy for water diffusion.

The propriety of reporting activation energies for the nontronite systems is open to question since only two or three points were available to establish the slopes of three of the four curves representing the first reaction. The slopes of the curves of the second portion of the Ni(phen)₃²⁺-nontronite experiments are better defined and yield a relatively low value for the apparent activation energy. The apparent activation energies re-

ported for the Upton smectite should be quite valid since the slopes of all the dehydroxylation curves are well established at two temperatures (Figure 1). The magnitude of the apparent activation energies for the Upton smectite systems is very compatible with those reported in the literature for smectites. The difference between the Ni²⁺- and Ni(phen)₃²⁺-montmorillonite of about 2000 calories is not very great. It appears that the presence of intercalated material has very greatly increased the velocity of the dehydroxylation process as exemplified by the relative magnitude of the rate constants but has not greatly influenced the apparent activation energy. This would suggest the basic process limiting the rate of reaction (perhaps diffusion) has not been changed by the presence of intercalate between the layers but that it has likely provided an avenue for more ready loss of water from the system, which permits the reaction described above to proceed more rapidly.

The isothermal studies on smectite dehydroxylation presented here were not designed to give rigorous answers to questions regarding mechanisms involved in this reaction. However, the results clearly show that the presence of a heat-stable intercalate has a marked influence in increasing the velocity of the dehydroxylation reaction.

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Резюме—Скорости дегидроксилирования смектитов, насыщенных продуктами разложения $\text{Ni}(\text{фен})_3\text{SO}_4$ от 2 до 4 раз выше, чем для глин без теплостойких прослоев. Эти результаты показывают, что эти включения, разделяя слои глины, обеспечивают лучшие условия для потери воды в течение процесса дегидроксилирования.

Resümee—Die Geschwindigkeiten der Dehydroxylierung von Smektiten mit eingelegten Zerfallsprodukten von $\text{Ni}(\text{phen})_3\text{SO}_4$, sind 2 bis 4 mal höher als die von Tonerden ohne die hitzebeständigen Einlagen. Diese Resultate schlagen vor, daß das eingeschobene Material, indem es die Tonschichten separiert, einen besseren Weg für den Verlust von Wasser während des Dehydroxylierungsvorgang verschafft.

Résumé—La rapidité de déhydroxylation de smectites intercalatés avec les produits de decomposition de $\text{Ni}(\text{phen})_3\text{SO}_4$ est de 2 à 4 fois plus élevée que celle d'argiles sans l'intercalate stable à l'échauffement. Ces résultats suggèrent que la matière intercalée fournit un chemin plus favorable à la perte d'eau pendant le processus de déhydroxylation en maintenant séparées les couches argileuses.