

SURFACE CHEMISTRY OF THERMALLY DECOMPOSED ORGANO-MONTMORILLONITE COMPLEXES

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Abstract—The hydrophilic-hydrophobic properties of four thermally decomposed organoclays, the octadecylammonium-, the dimethylaryloctadecylammonium-, and the dimethyldioctadecylammonium-bentonites and the dimethyldioctadecylammonium-hectorite, were examined through adsorption isotherms with nitrogen, water vapor, and hexane. Along with DTA and TGA results, these clay complexes appear to undergo transitions from low to higher degrees of hydrophilicity as more and more of the hydrocarbon chains are dehydrogenated at successive temperatures up to 400°C.

INTRODUCTION

IT HAS been well-established that organic compounds may interact with montmorillonites through either or both adsorption and ion exchange. When the organic substance is an ionic substance, such as a quaternary ammonium salt, the interaction is principally ion exchange (Slabaugh (1954), probably accompanied by interactions between the hydrocarbon chains and the clay's oxygen-populated surfaces as suggested by MacEwan (1948) and Green-Kelly (1956)).

Consequently, with the organic cation relatively fixed at the exchange sites and its hydrocarbon chains oriented in the interlaminal spaces, according to Jordan (1949), thermal degradation of the organic component can be achieved *in situ*. Recently, McAtee (1969) has shown that thermal decomposition of organo-clay complexes is essentially a removal of the hydrogen atoms from the hydrocarbon chain, leaving a deposit of carbon in the interlaminal spacing. This carbon is eventually removed at temperatures above 500°C as carbon dioxide when air is present or above 600°C in nitrogen along with the dehydroxylation of the clay substrate.

This study is concerned with an examination of the surface adsorption characteristics of partially decomposed organo-montmorillonites that have been heated to various temperatures ranging up to 400°C. It was primarily intended to explore the changes in the hydrophilic/hydrophobic nature of the clay surfaces as thermal decomposition progresses.

EXPERIMENTAL

Samples of prepared clay complexes obtained from the Baroid Division of the National Lead

Company Houston, Texas, served as starting materials. A selection of these materials is listed in Table 1. The clay complexes were extracted with 2-propanol for 24 hr in a Soxhlet extractor to remove any excess organic material. The resulting organoclays retained 90–95 m-equiv. organic cation per 100 g clay. After air-drying and gently grinding by mortar and pestle, samples of the clay complexes were heated to various temperatures both in air and in vacuum. In both methods of heating, considerable volatile material escaped from the sample, and its appearance changed. For example the sample of B-34 underwent the changes in weight and appearance as shown in Table 2 where the heating interval at each temperature was one hour and the sample was exposed to the air at all times.

Table 1. Composition of organo-clay complexes

Clay complex	Clay base	Organic group
B-18	Bentonite	Octadecylamine
B-24	Bentonite	Dimethylaryloctadecylamine
B-34	Bentonite	Dimethyldioctadecylamine
B-38	Hectorite	Dimethyldioctadecylamine

Adsorption isotherms on each of the samples were obtained with an eight-place gravimetric device previously described by Slabaugh and Stump (1964). This apparatus permits the observation of adsorption isotherms on eight samples concurrently. The nitrogen, water, and *n*-hexane were purified by standard techniques, and the isotherms for water vapor and hexane were analyzed by the B.E.T. method. The nitrogen areas were calculated by

Table 2. Changes in B-34 upon thermal decomposition in air

Temp. (°C)	Wt. of sample (g)	Appearance
25	1.00 (original)	white
50	0.99	white
100	0.99	white
150	0.99	white
200	0.99	pale-tan
250	0.98	gray-tan
300	0.92	medium gray
325	0.88	black
300	0.84	black
375	0.81	black
400	0.78	black

means of the Frankel-Halsey-Hill method as interpreted by Slabaugh and Stump (1964). Duplicate isotherms were made on each sample, and the data presented here are the averages of these two measurements.

Results of the isotherms, analyzed in terms of apparent surface areas, are summarized in Figs. 1-3. The areas per molecule of adsorbate were assumed to be: $N_2 = 16.4 \text{ \AA}^2$; $H_2O = 10.6 \text{ \AA}^2$; and $n-C_6H_{14} = 54 \text{ \AA}^2$.

Differential thermal and thermal gravimetric analyses were made on the original extracted samples. The DTA results are quite similar to those of McAtee and Chou (1969) for the same types of organoclays they examined. TGA results,

an example of which is shown in Fig. 4 for B-34, show that the clay complex loses weight only slightly up about 250°C, then undergoes a sharp decrease in weight between 250° and 500°C, and finally reaches a nearly constant weight at 800°C. The difference between TGA data in air vs. N_2 atmospheres is attributed to the presence of oxygen in the air atmosphere which probably oxidizes some of the organic component. Once this oxidation aspect begins, the system is stabilized at higher temperatures and the rate of weight loss in air is less than that in N_2 . A more definitive study of the crossover of these two curves at about 400° is needed to resolve this behavior because the present adsorption work extends only to 400°.

DISCUSSION OF RESULTS

The responses of the clay systems in terms of surface area measurements, as shown in Figs. 1-3, shows that thermal decomposition of the organic groups strongly affects their hydrophilic-hydrophobic character.

The nitrogen areas are essentially a measure of the external surface areas or those surfaces to which the nitrogen can adsorb without appreciably separating the individual clay platelets. It was somewhat surprising to note a sharp increase in the nitrogen areas for B-24 which had been preheated to 100°. All the clays presented a greater amount of nitrogen surface after preheating in the range above 300°C. This temperature corresponds to the beginning of carbonization of the organic groups, where the hydrocarbon chains begin to

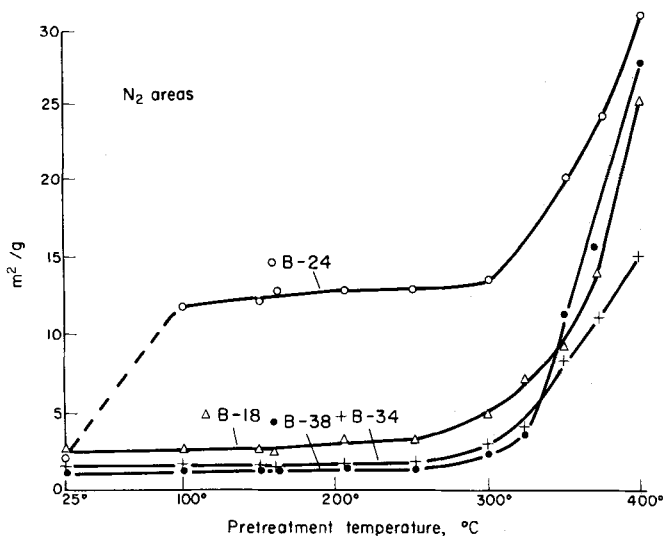


Fig. 1. Surface areas measured with nitrogen at -196°C , on samples thermally decomposed in air.

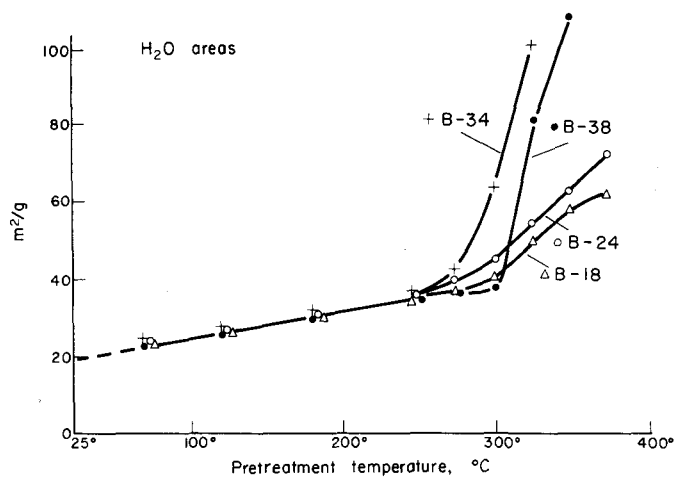


Fig. 2. Surface areas measured with water vapor at 25°C, on samples thermally decomposed in air.

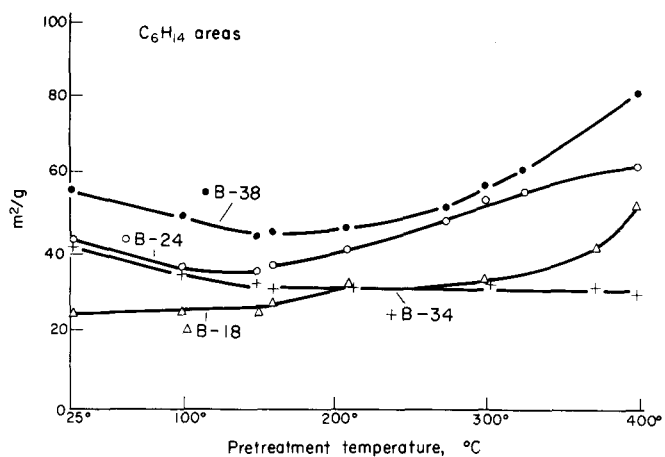


Fig. 3. Surface areas measured with n-hexane at 25°C, on samples thermally decomposed in air.

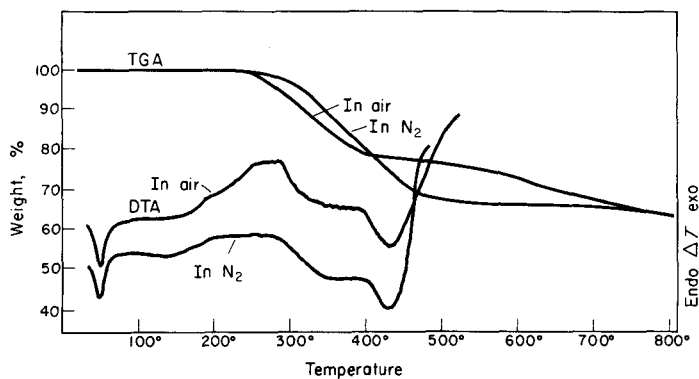


Fig. 4. Thermal gravimetric analysis and differential thermal analysis of B-34.

undergo dehydrogenation and the samples turn black. The hectorite organocomplexes started their darkening at some 25°C lower temperatures than did the montmorillonite complexes, indicating that the hectorite structure slightly favors the dehydrogenation step over the montmorillonite. This observation coincides with the McAtee and Chou (1969) report that montmorillonite's activation energy for the dehydrogenation step is higher than hectorites for the B-34 and B-38 systems.

The sharp rise in nitrogen areas following the preheating above 300°C is evidence that the clay platelets, now containing increasing amounts of carbon, remain separated enough to permit nitrogen to penetrate the interlaminar regions and adsorb onto both the inner surfaces of the clay as well as the carbon resulting from dehydrogenation.

Turning to the water vapor areas, one sees that the typical hydrophobic character of the organoclay is preserved up to 300°C, after which the thermal decomposition begins to change the clay system to a much more hydrophilic material. It is noted in Fig. 2 that the type of organic group is more influential in this conversion to hydrophilic nature than is the type of clay. Since carbon is relatively hydrophobic, the increase in hydrophilicity is attributed to more and more exposed clay surface (oxygen populated) as the hydrocarbon chains are dehydrogenated.

Finally, from the hexane adsorption data, thermal decomposition produces a slight but consistent decrease, followed by a somewhat greater

rise in surface areas, except with B-34. This is the organoclay that showed the greatest upturn in hydrophilicity when preheated at temperatures above 300°C. It is consistent that if this particular clay system becomes more hydrophilic at these conditions, it would also become less organophilic toward hexane. This is true for samples decomposed in both air and vacuum.

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Résumé—On a examiné, en mesurant les isothermes d'adsorption de l'azote, de la vapeur d'eau et de l'hexane, les propriétés hydrophiles-hydrophobes de quatre complexes organiques de l'argile décomposés thermiquement: les montmorillonites-octadécylammonium, -diméthylaryloctadécylammonium et -diméthylidioctadécylammonium, et l'hectorite-diméthylidioctadécylammonium. Parallèlement aux résultats de l'ATP et de l'ATG, ces complexes argileux semblent subir une transformation du caractère hydrophile qui, de faible devient élevé, au fur et à mesure que les chaînes hydrocarbonées sont déshydrogénées par des élévations successives de la température jusqu'à 400°C.

Kurzreferat—Die hydrophil-hydrophoben Eigenschaften von vier thermisch abgebauten Organotonen, den Oktadecylammonium-, Dimethylarlyloktadecylammonium-, und Dimethylidioktadecylammonium-Bentoniten und dem Dimethylidioktadecylammonium-Hektorit wurden untersucht durch Adsorptionsisotherme mit Stickstoff, Wasserdampf und Hexan. Mit den DTA und TGA Ergebnissen, scheinen diese Tonkomplexe Übergänge von niedrigen auf höhere Stufen von Hydrophilizität zu erfahren in dem Masse als mehr und mehr Kohlenwasserstoffketten bei steigenden Temperaturen bis zu 400°C dehydriert werden.

Резюме—С помощью анализа изотерм адсорбции азота, водяного пара и гексана проведено исследование гидрофильных и гидрофобных свойств четырех термически разложенных органоглин: октадециламмоний-, диметиларилоктадециламмоний- и диметилдиоктадециламмоний-бентонитов и диметилдиоктадециламмоний-гекторита. В соответствии с данными ДТА и ТГА, степень гидрофильности этих глинистых комплексов меняется от низкой к высокой по мере того как все большая и большая часть углеводородных цепей дегидрогенизируется при постепенном повышении температуры до 400°C.