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INVERSE GAS CHROMATOGRAPHY STUDY OF MODIFIED SMECTITE SURFACES

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Abstract—Inverse gas chromatography at infinite dilution, employing alkanes and alkenes as probes, has been used to characterize the surface properties of a series of smectites of varying chemical composition. The results of this study show that the acidic centers and the interlayer distances have a great influence on the specific interaction of the smectite surface with π-bonds of alkenes. High values of the specific interaction parameter, ϵ_π, are caused by the existence of strong acidic centers that are connected with interlayer cations as well as with the chemical structure of the mineral sheets. On the other hand, alkanes, whose interaction with the smectites is predominantly dispersive, are unaffected by changes in the clays' composition and/or structure.

Key Words—Smectite, Intercalation, Inverse gas chromatography, Alkane and alkene sorption, Surface acidity, Surface energy.

INTRODUCTION

The intercalation of smectites with hydroxy-metal polycations is a method of mineral modification developed in the late 1970's (Brindley and Sempels, 1977; Lahav *et al.*, 1978; Vaughan *et al.*, 1979). The method involves the introduction of large metal polycations into the interlayer spaces of clay minerals using ion exchange from aqueous solutions. The polycations act as "pillars" supporting the layers and additionally, after calcination, make the structure rigid. After heating treatment the hydroxycation "pillars" are converted into oxide "pillars" (Occelli and Tindwa, 1983). The intercalated smectite is characterized by large specific surface area, developed porous structure, and high surface acidity (Lahav *et al.*, 1978; Vaughan *et al.*, 1979; Occelli and Tindwa, 1983; Brindley and Yamanaka, 1979). Because intercalated smectite also has high thermal resistance, it has application in a variety of chemical processes as a catalyst or catalyst carrier. In addition, it shows promise as a molecular sieve and sorbent (Occelli and Tindwa, 1983; Pinnavaia, 1983; Diddams *et al.*, 1984).

The sorbent properties of smectites depend on the manner of modification of the initial mineral, and on the heat treatment of the resulting product. Many studies in the literature have been devoted to the study of the surface properties of clay minerals (Brindley and Kao, 1980; Yamanaka and Brindley, 1979; Yamanaka *et al.* 1984). Such properties are of importance when these materials are used as catalysts (Diddams *et al.*, 1984; Kikutchi *et al.*, 1985), adsorbents, or as reinforcing fillers.

In our laboratory we have applied chromatographic methods to determine the surface properties of wide classes of materials. It is the objective of this study to present the results of applying the inverse gas chromatographic method at infinite dilution, and to demonstrate that this method provides a convenient way to evaluate surface properties of clay minerals. We show that by using alkane in conjunction with alkene molecular probes, we can determine such surface properties as the acidity, the dispersive component of the surface free energy, and the surface area of a mineral. The advantages of this method are speed, reliability of measurements, and direct thermodynamic interpretation of the experimentally derived parameters.

Inverse gas chromatography at infinite dilution

Gas-solid chromatography is called inverse gas chromatography (Gilbert, 1984) when applied to the investigation of solid surface properties. This method is based on the study of interactions of gas molecules of known properties with solid surface. Small amounts of molecular probes are injected into the stream of the carrier gas flowing through the chromatographic column filled with the solid to be investigated. The net retention time t_N is measured as a difference between retention times of a given probe and a non-adsorbing gas used as a reference. The net retention volume, V_N, which is the fundamental quantity utilized in this method, is calculated from the formula

$$V_N = jFt_N, \quad (1)$$

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where j is the James-Martin compressibility factor and F is the flow rate of the carrier gas.

It is assumed in the case of infinite dilution chromatography that the adsorption is described by Henry's law and hence we can write

$$V_N = mKS, \quad (2)$$

where m is mass, S is specific surface area of adsorbent, and K is Henry's constant. Since the surface of an adsorbent is usually energetically heterogeneous, Henry's constant is considered as a mean value of K° which is related to different adsorption sites. This yields

$$K = \int_{\epsilon_l}^{\epsilon_m} K^\circ(\epsilon)\chi(\epsilon)\, d\epsilon, \quad (3)$$

where $\chi(\epsilon)$ is the distribution of adsorption energy, ϵ, in the domain (ϵ_l,ϵ_m) and K° is the Henry's constant for adsorption sites having energy ϵ.

The standard free energy of adsorption at infinite dilution is directly related to the net retention volume, V_N (Kiselev and Yashin, 1969):

$$\Delta G^\circ = -RT \ln\frac{BV_N}{Sm}, \quad (4)$$

where R and T are the gas constant and temperature, and B is a constant related to the standard states of gas and adsorbed phases. Values of ΔG° obtained under the conditions of infinite dilution are dependent on the interaction of probe molecules with the surface only; interaction between adsorbed molecules are neglected.

Analysis of ΔG° values obtained for appropriate molecular probes can provide information about surface properties. In general adsorbate-adsorbent interactions can be classified as dispersive (non-specific) or polar (specific). Among probes which can undergo only dispersive interactions, n-alkanes are of great practical importance. Values of the free energy, ΔG°, for n-alkanes are directly related to the number of carbon atoms, n, in the structure. This behavior was adopted by Dorris and Gray (1980) to calculate the dispersive component of the surface free energy, γ_s^D, using equation

$$\gamma_s^D = \frac{1}{\gamma_{CH_2}}\left[\frac{\Delta G_{CH_2}}{2Na_{CH_2}}\right]^2. \quad (5)$$

ΔG_{CH_2} is the difference in the ΔG° of two subsequent n-alkanes, N is Avogadro's number, a_{CH_2} is the surface area of a CH_2 group and γ_{CH_2} is the surface energy of a hypothetical surface made of CH_2 groups only (e.g., polyethylene). The value of ΔG_{CH_2} is obtained from the slope of ΔG° versus the number of carbon atoms in the alkane.

When chromatographic measurements are performed at several temperatures, the enthalpy of adsorption at infinite dilution ΔH° is calculated by

$$\Delta H^\circ = -R\frac{\partial \ln(V_N)}{\partial(1/T)}. \quad (6)$$

Alkanes have also been used in conjunction with unsaturated and aromatic hydrocarbons to study specific interactions of different surfaces in terms of the enthalpy of adsorption (Belyakova *et al.*, 1970). Recently Sidqi *et al.* (1989) proposed to compare ΔG° values of n-alkenes and n-alkanes to study the effect of the π bond interactions with electron acceptor sites on the surface. The specific interaction parameter, ϵ_π, is defined by

$$\epsilon_\pi = \Delta G^\circ_{alkane} - \Delta G^\circ_{alkene}. \quad (7)$$

Based on the well-known electronic structure of alkanes and alkenes, this parameter can be taken as a measure of the specific (electron acceptor) interaction capacity of the surface.

When the experimental conditions are maintained constant, the dispersive interaction parameter, ΔG_{CH_2}, and the specific interaction parameter, ϵ_π, are, according to their definitions, obtained directly from the ratios of appropriate retention times, t_N.

EXPERIMENTAL

Materials

The clay fraction (<2 μm) of a Wyoming bentonite was separated from the bulk sample in a settling tube. Then the smectite clay fraction was saturated with 1 N NaCl to obtain Na-smectite for ion exchange with hydroxy-aluminum cations. The solution of hydroxy-aluminum oligocations was prepared by adding NaOH to $AlCl_3$ solution and then stirring the mixture to prevent local precipitation of $Al(OH)_3$. The size of oligocations was controlled by making a solution with an OH/Al ratio of about 2.5 (Vaughan *et al.*, 1979). The oligocation solution was mixed directly with a water suspension of smectite in order to exchange hydroxy-aluminum cations with sodium cations. The modified smectite was washed with distilled water until $AgNO_3$ test for Cl^- was negative. The sample was then dried on a water bath and heated at 673 K for 10 hours. The intercalated sample is designated ISAl and the calcined intercalated sample is designated ISAl-C.

Inverse gas chromatography

The chromatographic experiments were performed with an ANTEK 3000 gas chromatograph (from Antek Instruments Inc.) with a flame ionization detector. The stainless steel columns of 2.17 mm in diameter were used, 20 cm long for intercalated forms and 50 cm for sodium form; the particle granulation was 0.2–0.4 mm and the amount of adsorbent was in the range of 1–2 grams. Helium at a flow rate of 30 cm^3/min was used as a carrier gas; it was dried by passing through a molecular sieve trap. The injector and detector temperatures were 383 K and 493 K. The samples were conditioned at 473 K in the helium gas flow for 15 hr prior to the measurements. The hydrocarbons used for in-

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Table 1. Inverse gas chromatography results at 453 K.

Sample	Parameter of specific interactions $\epsilon_\pi(4)$ [kJ/mol]	Parameter of dispersive interactions ΔG_{CH_2} [kJ/mol]	Dispersive component of surface energy γ_s^D [kJ/mol]	Specific retention volume for hexane V_N/m [cm³/g]
Na-S	4.44 ± 0.1	4.68 ± 0.1	159 ± 3	21 ± 1
ISAl	3.88 ± 0.1	4.85 ± 0.1	171 ± 3	263 ± 13
ISAl-C	2.45 ± 0.1	4.70 ± 0.1	160 ± 3	68 ± 3

jections were HPLC grade (Aldrich Chemical Co.). Size of injections was about 10 μl of vapor solutes. The experiments were done in the range of temperature 423–623 K and all chromatographic peaks were symmetrical and retention times did not depend on the amount injected (Henry's law region). Each new injection was done only after the base line was stabilized. Retention volumes were corrected for the gas compressibility. The error of the measurement of retention time was 5% and the temperature was stabilized with an accuracy ±0.1 K.

X-ray analysis

Oriented clay mounts were made by settling a suspension of smectite onto a glass slide. All clay mounts were dried at room temperature and heat treated clay mounts were rehydrated after calcination at 673 K. X-ray diffractograms were produced with Philips PW1729 diffractometer using filtered CuKα radiation. The measured d_{001} spacings and calculated interlayer spacings are reported in Table 2.

RESULTS AND DISCUSSION

The important features of clay minerals and their modified forms are surface area, the pore structure, and the chemical character of the surface. We find our gas chromatographic results are related to these properties (Table 1). The variation of the retention volumes of different alkanes and alkenes of selected samples illustrates the principles of the method which we have applied in this study (Figure 1). The values for alkenes are higher than the values for alkanes due to specific interactions with electron acceptor surface sites (acidic sites). For Na-S, the curves are almost parallel, whereas for ISAl-C the difference between alkenes and alkanes slightly decreases. We adopt here ϵ_π values defined by Eqs. (7) or (8) as a measure of the contribution of the specific interaction with electron acceptor surface sites (Jagiełło *et al.*, 1992). The values in Table 1 are calculated from butane and butene results at 453 K. This choice was based on the fact that we have observed some cracking effects at higher temperatures and for longer unsaturated carbons.

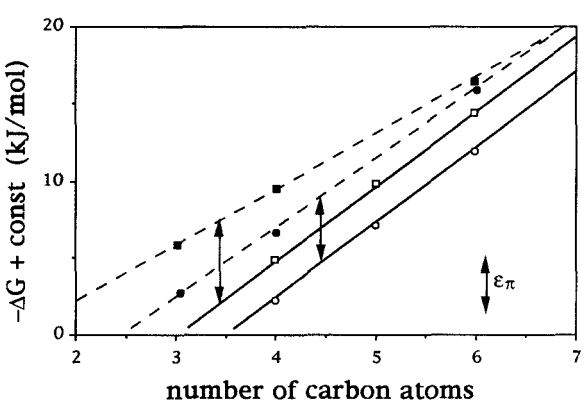


Figure 1. ΔG° versus number of carbon atoms in alkane (open symbols) and alkene (filled symbols) adsorbed on Na-S (circles) and ISAl-C (squares) at 453 K.

The surfaces of clay minerals are known to have strong acidic properties (Lahav *et al.*, 1978; Vaughan *et al.*, 1979; Occelli and Tindwa, 1983; Brindley and Yamanaka, 1979) which are related to layer defects, interlayer material, and OH^- groups and oxygen atoms from the silicate layer. Cations of interlayer material and silicate layers form very strong Lewis acid centers.

The results of ϵ_π which are used to evaluate the acidic properties of our samples are presented in Table 1. The highest value of ϵ_π is obtained for Na-smectite which is due to very strong specific interactions of the double bond (π-electrons) of alkenes with metallic cations playing the role of Lewis acid sites. In the Na-smectites these cations are accessible for alkene molecules only on edges and on external surfaces of sheets of the mineral since the sorbate molecules are too big to enter the interlayer space which is only 0.36 nm (Table 2; Barrer, 1978).

After intercalation, the interlayer distance of smectite increases to about 1.7 nm (Table 2; Vaughan *et al.*, 1979; Occelli and Tindwa, 1983; Zyła and Bandosz, 1987). As a result of intercalation, however, ϵ_π decreases. This can be explained by the fact that alkane molecules interact mainly with Bronsted acid sites related to pillaring hydroxy-cations (Vaughan *et al.*, 1979; Occelli and Tindwa, 1983), which are weaker acids compared to metallic cations. The smallest value of ϵ_π is obtained for the ISAl-C sample. This significant decrease of acidic properties is caused by chemical changes

Table 2. X-ray diffraction results.

Sample	Interlayer space [nm]	d_{001} [nm]
Na-S	0.36	1.24
ISAl	0.72	1.70
ISAl-C	0.62	1.60

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of the interlayer material (Vaughan *et al.*, 1979; Occelli and Tindwa, 1983).

After calcination, the hydroxy-aluminum pillars are transformed into aluminum oxide pillars. The interactions of these Lewis centers with π-bonds are smaller than those of metallic cations or OH^- groups. The result is a decrease in ϵ_π values versus the number of carbon atoms (Figure 1). This can be explained by the fact that in the narrow interlayer space of the calcined smectite the longer alkene molecules may have difficulty in reaching an optimum position during interaction with active acidic sites. Similar effects have been observed by Ligner *et al.* (1990) for crystalline layer silica.

On the other hand, results of γ_s^P and ΔG_{CH_2} show that these values which represent dispersive (non-specific) components of the surface free energy, are unaffected by the modification process. The internal and external surface of smectite are very similar from the point of view of non-specific interactions.

The modification process changes the measured specific retention volumes, V_N/m, for hexane calculated per gram of adsorbent (Table 1). The effect of modification of Na-smectite by introduction of hydroxy-aluminum pillars is reflected by the increase of the specific retention volume for ISAl smectite by more than an order of magnitude compared to the untreated smectite. In our case, since the surface energy γ_s^P is practically constant, we can assume that Henry's constant in Eq. (3) is also unchanged. This implies that according to Eq. (3), V_N/m is proportional to the specific surface area of the adsorbent. Therefore, the intercalation causes the increase of the specific surface area by a factor of 10 which is in agreement with the results obtained by Vaughan *et al.* (1979) and Occelli and Tindwa (1983). Using the same argument for the calcined smectite, ISAl-C, we see that surface area after calcination decreases, most likely as a result of a partial collapse of the interlayer pillars.

The above discussion is based on isothermal results at a common temperature (453 K). We have also performed experiments at other temperatures in order to calculate adsorption enthalpies (Figure 2). We observe the typical linear variations of $\Delta H°$ versus number of carbon atoms of alkanes (Kiselev, 1967). Adsorption enthalpies of alkanes represent only the dispersive interaction energy with the surface. The constancy in these values, similar to γ_s^P and ΔG_{CH_2}, demonstrates that this energy is not considerably changed by modification of smectite. Values of $\Delta H°$ for alkenes represents both dispersive and specific interactions of alkenes with the surface of smectite. The net specific interaction enthalpy, ΔH_π, is related to the additional interactions with π-bonds. For the parameter, $\Delta H_\pi = \Delta H°_{alkane} - \Delta H°_{alkene}$, we have obtained values scattered about 10 kJ/mol. These values are of the same order of magnitude as those obtained by Kiselev (1967) for

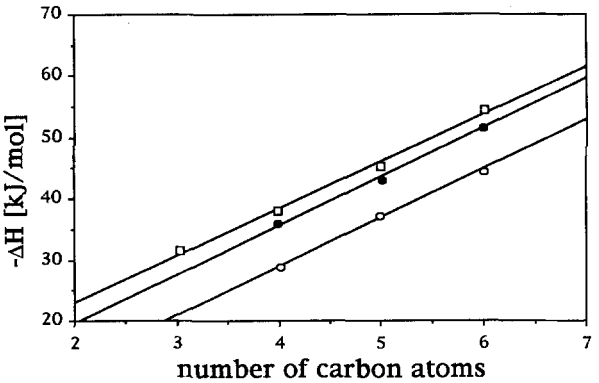


Figure 2. Dependence of ΔH of alkane adsorption versus number of carbon atoms measured for Na-S (O), ISAl-C (●) and ISAl (□) at 453 K.

$BaSO_4$ and Ashan *et al.* (1989) for $CaCO_3$. However, changes in ΔH_π values for the smectite series are within the experimental error which we estimated to be ± 3 kJ/mol. Therefore we cannot discuss the results obtained for this quantity in terms of the effects of either intercalation or calcination.

CONCLUSION

Our inverse gas chromatography study of smectite demonstrates that this is a useful method, complementing traditional spectroscopic studies, for measuring the surface properties of lamellar clay minerals. Simple molecular probes such as alkanes and alkenes can be used to determine the dispersive and specific (acidic) interaction characteristics of smectite. In addition, results from this method are sensitive to changes in surface properties of interlamellar complexes after modification by intercalation and calcination.

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