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THERMAL ANALYSIS OF COMPOUNDS ADSORBED ON LOW-SURFACE-AREA SOLIDS. PART 1. MEASUREMENT AND CHARACTERIZATION BY TGA

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ABSTRACT

Thermogravimetric analysis (TGA) was applied to the investigation of organic molecules adsorbed on low-surface-area minerals (less than one square meter per gram). The weight loss was used to quantify the adsorbed material; typical losses were of the order of 0.1 wt.% (8 μg) and were reproducible to within 0.02 wt.%. This level of precision easily allowed the identification of monolayer coverage. The temperature at which the weight loss occurred provided a convenient indication of the strength of the adsorption.

INTRODUCTION

In this work, thermogravimetric analysis (TGA) was applied to the measurement and characterization of adsorbates on low-surface-area materials because a rapid procedure was required to scan a wide variety of potential adsorbates. Our aim was to determine the chemical and structural properties of organic compounds that adsorb strongly on carbonate minerals.

TGA provides a quantitation of the adsorbed material as well as a measure of the strength of the adsorption. TGA was chosen over other techniques (such as spectroscopy) because it can be applied to all organic adsorbates; it does not require aromaticity or a certain functional group for detection. An additional advantage of TGA is that it directly measures the material adsorbed on the solid; it is not subject to the losses that must be addressed when solid coverage is determined from differences in solution concentrations.

Thermogravimetry has been used previously to quantify adsorbed organics [1–4]; however, previous investigations have been limited to high-surface-area substrates such as catalysts. In this work, adsorption on low-surface-area minerals (below 1 m^2 g^{-1}) was studied. In addition, the temperature of the weight loss was correlated with other indications of the strength of the adsorption. Gabelica et al. [3] have interpreted TGA curves to indicate that weakly adsorbed species exhibit weight losses at lower temperatures than chemisorbed species. Our results agree with this.

EXPERIMENTAL

The calcite substrate used was calcium carbonate reagent-grade primary standard from Mallinckrodt. The powder was examined by scanning electron microscopy before and after contact with adsorbate solutions, and no visible differences were observed. The particles were well crystallized, with dimensions of approximately 3 μm. X-ray diffraction analysis showed pure calcite. The BET surface area measured by nitrogen adsorption was 0.60 m^2 g^{-1}. TGA runs on the as-received calcite powder showed no weight loss below 580 °C.

Three adsorbates are presented in this paper. Triacontanoic acid and stearyl alcohol were both obtained from Sigma (99%). Stearic acid was obtained from Fisher (reagent grade). The solvents used to apply the adsorbates were toluene (Fisher, cert. ACS), heptane (Fisher, reagent) and isopropanol (Baker, reagent, ACS).

Each TGA sample was prepared by stirring 1.000 g or 0.500 g of calcite power in 50 ml of a solution containing the adsorbate for 30 min. This was performed in a 100 ml beaker with a 1 in stir bar. The stirring rate was always fast enough to suspend the adsorbent powder, and 30 min was determined to be an adequate contact time by comparison with other contact times. The initial solution concentrations of adsorbates ranged from 0.010 wt.% to 1.0 wt.%. After stirring, the mixture was divided. Approximately half of the powder was filtered and allowed to air dry on the filter paper overnight. It was found that hardened filter paper was optimal for avoiding contamination of the powder with filter paper fibers. To assess the reversibility of the adsorption, the other half was filtered and then washed in the funnel with three to five washes of pure solvent. The wash solvent was the same as that used for the adsorption. Each wash totally immersed the powder and was allowed to drain completely before the next wash. This sample was then allowed to air dry on the filter paper overnight.

Thermogravimetric analyses were performed with a Perkin–Elmer model TGS-2. Each sample weighed about 8 mg, and a heating rate of 10 °C min^{-1} was used. Compressed building air (purified to remove particulates and oil) was used to purge the furnace tube at 40 cm^3 min^{-1}. Data were analyzed on a Perkin–Elmer model 3600 data station with the Perkin–Elmer software provided for that purpose. Low noise levels (3 μg peak to peak) enabled measurements to be made of the small losses arising from volatilization or combustion of the organics.

RESULTS AND DISCUSSION

Thermogravimetric analyses were run on samples of calcite powder after they had been treated with a solution of organic adsorbate. The weight of the sample was followed as a function of temperature, and a weight loss was observed when the organic left the sample. In the 100 TG analyses that were performed for organic adsorbates on carbonate minerals, the weight losses fell into two fairly distinct temperature ranges. These different temperatures are interpreted as follows: low-temperature losses (below about 250 ° C) indicate volatilization (desorption) of the organic without the disruption of any chemical (intramolecular) bonds; high-temperature weight losses (above about 250 ° C) occur when the organic molecule combusts or decomposes before it desorbs from the surface. Thus, low-temperature weight losses indicate a weak, physical adsorption, and high-temperature weight losses indicate a strong, chemical or ionic adsorption. These interpretations were confirmed by studies of the reversibility of the adsorption. Low-temperature losses correlate with easily reversible adsorption, and high-temperature losses correlate with fairly irreversible adsorption. Our choice of 250 ° C as the cut-off between physical and chemical adsorption is approximate, and it will vary with changes in the instrument, gas stream, sample size or heating rate.

From the magnitude of the weight loss, we quantified the amount of organic material on the surface. Theoretical calculations of monolayer coverage were approached from two standpoints: the close-packed arrangement of the adsorbate and the surface density of calcium ions on the crystal faces of calcite. For fatty acid adsorption on calcite, the surface area per adsorbate molecule and the surface area per calcium ion agree very well. Fatty acids are generally assumed to occupy 20.5 $Å^2$ per molecule when oriented perpendicular to a surface [5]. The four dominant faces of calcite and their surface areas per calcium ion are given in Table 1. The surface area range is 16–25 $Å^2$, and the average value of 20.8 $Å^2$ is very close to the 20.5 $Å^2$ for close-packed fatty acids. The value of 20.8 $Å^2$ was used to calculate monolayer coverage because it is more likely that the organic molecules can

TABLE 1

Dominant calcite faces and their areas per calcium ion [a]

Face	Hexagonal indices	Surface area per calcium ($Å^2$)
c	001	21.5
m	100	21.5
a	110	24.5
p	101	15.8

[a] Based on cell dimensions of $a_0 = 4.98$ Å and $c_0 = 17.02$ Å [6].

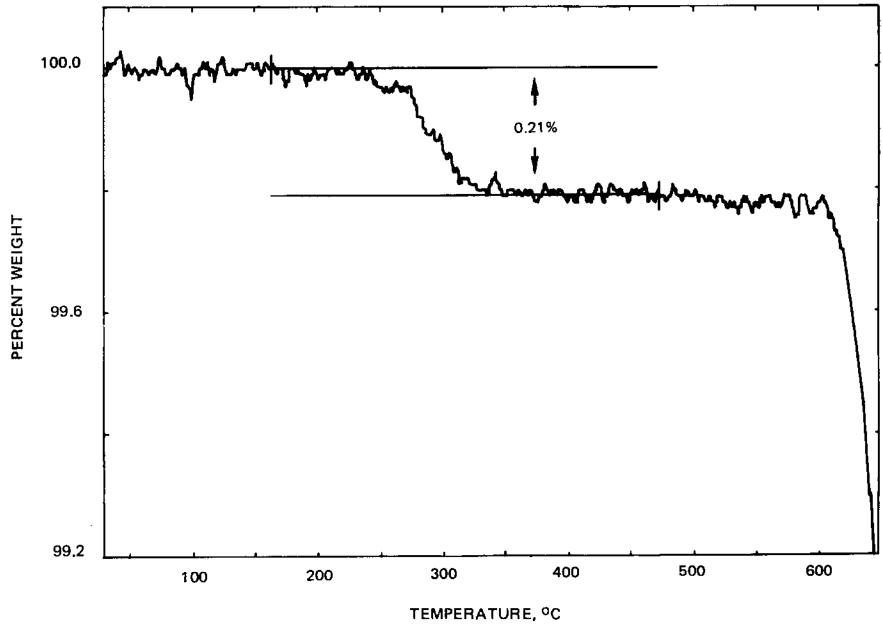

Fig. 1. Thermogravimetric analysis of triacontanoic acid adsorbed on calcite from toluene. The sample was washed with toluene. The weight loss occurs from 240–350 ° C and corresponds to 7.7 μmol m^{-2}.

accommodate the calcium spacing than vice versa. This results in a monolayer coverage of 8.0 μmol m^{-2} for these organics on calcite.

Examples of TGA curves are given in Figs. 1 and 2. Figure 1 shows a high-temperature weight loss for triacontanoic acid. The weight loss of 0.21% corresponds to a coverage of 7.7 μmol m^{-2}, which is within the experimental uncertainty of the theoretical monolayer. Figure 2 shows a low-temperature weight loss for stearyl alcohol. The 0.13% weight loss indicates a surface coverage of 8.0 μmol m^{-2}, in excellent agreement with the theoretical monolayer coverage.

Sometimes weight losses are observed at both high and low temperatures. The high-temperature loss corresponds to a monolayer of the adsorbate, and the low-temperature loss is interpreted as corresponding to additional adsorbate physically adsorbed (condensed) on top of the monolayer. Figure 3 shows a TGA curve for stearic acid that demonstrates this behavior. The low-temperature weight loss occurs over the same temperature range as does the volatilization of pure stearic acid under the same conditions in TGA (140–240 ° C). This supports the idea that the low-temperature loss reflects the intermolecular interactions of stearic acid with itself rather than with the calcite surface. The high-temperature weight loss of 0.12% indicates a surface coverage of 7.1 μmol m^{-2}. This is within the experimental uncertainty of the theoretical monolayer coverage, and it results from stearic acid adsorbed directly on the calcite surface.

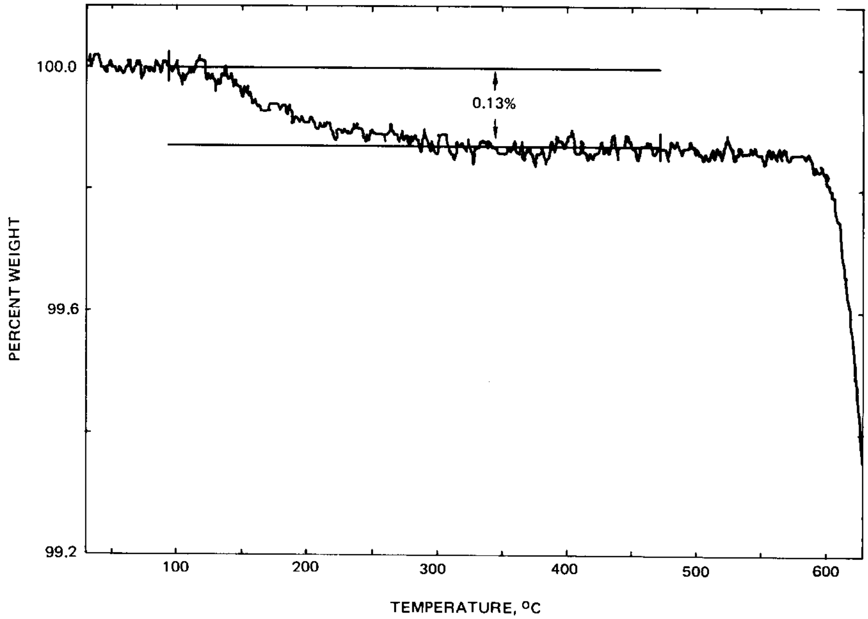

Fig. 2. Thermogravimetric analysis of stearyl alcohol adsorbed on calcite from heptane. The sample was not washed. The weight loss occurs from 130–270 °C and corresponds to 8.0 μmol m^{-2}.

The interpretations of low-temperature weight losses as physisorption and high-temperature weight losses as chemisorption were substantiated by our studies of reversibility. The low-temperature stearyl alcohol and stearic acid were readily desorbed by washing the powder with heptane and isopropanol, respectively. The ease of removal indicates a physical adsorption with intermolecular interactions only. The high-temperature losses for triacontanoic acid, stearic acid and other fatty acids were unaffected by washes with heptane, toluene or water, although they were desorbed by alcohols and aqueous–organic mixed solvents. Removal of the fatty acid monolayers required a solvent that could provide both adequate solubility for the fatty acid and an ion that could replace it at the calcite surface. The latter requirement indicates that the fatty acids (actually the fatty acid anions) chemisorb to the calcite surface with an ionic bond. When the adsorption takes place from a hydrocarbon solvent, the dissociation of the acid probably takes place at the calcite surface. The anion(s) adsorbs, and the proton(s) may combine with a displaced carbonate, bicarbonate or hydroxide to form a neutral species with some solubility in the hydrocarbon solvent.

The accuracy of thermogravimetric analysis applied to adsorption depends on the substrate's surface area, the adsorbate's molecular weight and orientation and the instrument's sensitivity to and analytical capabilities for small weight changes. As previous studies have demonstrated, very good

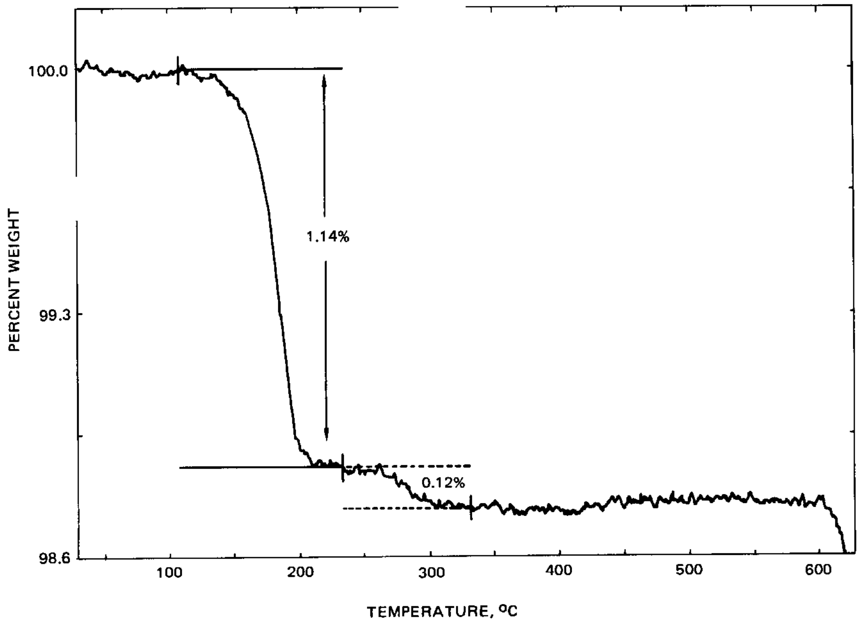

Fig. 3. Thermogravimetric analysis of stearic acid adsorbed on calcite from isopropanol. The sample was not washed. The low-temperature weight loss occurs from 120–210 °C. The high-temperature weight loss occurs from 260–320 °C and corresponds to 7.1 μmol m^{-2}.

accuracy is achievable for a variety of adsorbates when the substrate has a high surface area (greater than about 50 m^2 g^{-1}). With low-surface-area substrates, such as the calcite used in this study, the long-chain organics that orient themselves perpendicular to the surface are ideal adsorbates because they provide a large weight loss per unit surface area. With these adsorbates, we were able to measure weight losses of 0.1 wt.% with a reproducibility of 0.02 wt.%, which is adequate to identify monolayer coverage. Low-molecular-weight adsorbates or adsorbates that orient themselves parallel to the substrate surface may not yield sufficient weight losses for detection by TGA. Of course, it is also necessary to have a thermobalance that is sensitive to small weight losses, and analytical capabilities (such as computerized data storage and handling) that allow one to expand the weight scale and quantify small weight changes.

Detection of adsorption by TGA obviously requires that the adsorbate volatilize before the substrate does. Because of the sensitivity required for the analysis, this is particularly important for low-surface-area materials. It is necessary that the substrate is pure and free of any weight losses in the temperature region of interest. Non-hygroscopic, reagent-grade materials generally meet this criterion, but many natural rocks and minerals do not. The suitability of a substrate can easily be evaluated by TGA of the pure substrate.

For appropriate substrates and adsorbates, thermogravimetry provides a rapid and accurate measure of adsorption. It offers an advantage over several other adsorption measurements because it directly measures the surface concentration rather than deducing it from differences in solution concentrations. Thus, it is not particularly sensitive to errors that arise from adsorption on equipment. It has not been applied previously to low-surface-area materials, but it has been demonstrated here that it can be used successfully to assess the adsorption of organic compounds on calcite. It should apply equally well to many other adsorption studies, particularly those that pertain to the adsorption of surface-active organics on pure substrates.

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