Thermogravimetric analysis of tetradecyltrimethylammonium bromide-modified beidellites

**Yet Hong Lim · Balázs Zsirka · Erzsébet Horváth ·
Janos Kristóf · Sara Couperthwaite ·
Ray L. Frost · Godwin A. Ayoko · Yunfei Xi**

Abstract The surfaces of natural beidellite clay were modified with cationic surfactant, tetradecyltrimethylammonium bromide, at different concentrations. The organo-beidellites were analysed using thermogravimetric analysis which shows four thermal oxidation/decomposition steps. The first step of mass loss is observed from room temperature to 130 °C due to the dehydration of adsorbed water. The second step of mass loss between 130 and 400 °C is attributed to the oxidation step of the intercalated organic surfactant with the formation of charcoal. The third mass loss happens between 400 and 500 °C which is assigned to the loss of hydroxyl groups on the edge of clays and the further oxidation step of charcoal. The fourth step is ascribed to the loss of structural OH units as well as the final oxidation/decomposition step of charcoal which takes place between 500 and 700 °C. Thermogravimetric analysis has proven to be a useful tool for estimating loaded surfactant amount.

Introduction

The smectite group of clay minerals represent the most important phyllosilicates which are widely used in a range of applications because of their cation exchange capacities, high surface areas and resulting high adsorption capacities. Though both montmorillonite and beidellite belong to the smectite group, montmorillonite is one of the most studied clay minerals. There are numerous papers on the properties of organic surfactant-modified montmorillonites [1–8]. In common with montmorillonite, beidellite consists of 2:1 TOT layers with the ideal formula of $[Si_{3.5}Al_{0.5}][Al_2]O_{10}(OH)_2Ca_{0.25}$ [9, 10]. However, the property and the potential application of beidellite have received less attention [11]. The net negative surface charge on some beidellites mainly originates from the isomorphous substitution of Al^{3+} for Si^{4+} in the silicate tetrahedral sheets [9], while the charge of montmorillonite is usually from the octahedral substitution of Al^{3+} by Mg^{2+}. Because of this substitution, the surface charge is regular as opposed to random as for montmorillonite.

To the best of our knowledge, compared with montmorillonite, there are fewer studies on organo-beidellites and their thermal properties have sparsely been reported in the literature. Hence, the present research is aimed to examine the thermal properties of organo-beidellites. Thermogravimetric measurement was used to characterize the thermal oxidation and decomposition of tetradecyltrimethylammonium bromide-modified beidellites prepared at different surfactant concentrations and to estimate the loaded surfactant amounts within organo-beidellites.

Y. H. Lim · S. Couperthwaite · R. L. Frost ·
G. A. Ayoko · Y. Xi (✉)
School of Chemistry, Physics and Mechanical Engineering,
Queensland University of Technology, 2 George Street,
GPO Box 2434, Brisbane, QLD 4000, Australia
e-mail: y.xi@qut.edu.au

B. Zsirka · E. Horváth · J. Kristóf
Institute of Environmental Engineering, University of Pannonia,
P.O. Box 158, Veszprem 8201, Hungary

Materials and methods

The SBId-1 beidellite clay, obtained from Clay Minerals Repository USA, has a cation exchange capacity (CEC) of 129 meq/100 g [12]. The surfactant selected for this study, tetradecyltrimethylammonium bromide (denoted as TDTMA, $C_{17}H_{38}NBr$, FW: 336.39), was obtained from Sigma-Aldrich. All materials were used as received without purification (Fig. 1).

Synthesis of organo-beidellite was undertaken by the following procedure: beidellite sample was finely grounded with an agate mortar and then sieved through a 250-μm sieve. Four gram of beidellite was dispersed into 400 mL of deionized water. The clay suspension was stirred at 600 rpm for an hour using a magnetic stirrer. Stoichiometric amount of 25 % (0.25 CEC), 50 % (0.50 CEC), 75 % (0.75 CEC), 100 % (1.00 CEC) and 125 % (1.25 CEC) of TDTMA was slowly added to the clay suspension and stirred at 600 rpm at room temperature for another 3 h. The mixture was allowed to settle overnight and the supernatant was decanted. All organo-clays were washed with high-purity water until free of bromide anions as determined by $AgNO_3$ test. All samples were dried at room temperature and stored in plastic sample containers in a vacuum desiccator. The prepared TDTMA-modified beidellites, with surfactant loadings corresponding to CEC values from 0.25 to 1.25, were denoted as 0.25CEC-TB, 0.5CEC-TB, 0.75CEC-TB, 1.00CEC-TB and 1.25CEC-TB, respectively.

Thermogravimetric analyses of the TDTMA-modified beidellites were carried out in a Netzsch TG-209-type thermobalance in a ceramic crucible up to 1,000 °C. The samples were heated in an atmosphere containing 20 % O_2 and 80 % Ar (99.995 % purity) at a rate of 10 °C min^{-1}.

Results and discussion

TG and DTG curves of the organo-beidellites are presented in Fig. 2. Generally, there are four main mass loss steps which are observed for each organo-beidellite. The first mass loss occurring from room temperature to about 130 °C is related to the loss of adsorbed water. The second mass loss, in
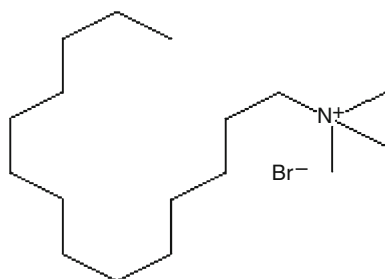

Fig. 1 Molecular structure of tetradecyltrimethylammonium bromide

the temperature range 130–400 °C, corresponds to the first thermal oxidation/decomposition step of TDTMA surfactant which was oxidized to H_2O and CO_2 with the formation of charcoal residue. The third mass loss at around 400–500 °C is presumably due to the loss of OH units at the edge of clay layers [13] as well as the oxidation step of charcoal, which persisted at about 420 °C and then was gradually oxidized by air [14], while the mass loss at around 500–700 °C is due to the final oxidation of the residue charcoal in the clay and the dehydroxylation of the structural OH units. A very small mass loss recorded at about 530 °C only for 0.25CEC-TB may also be due to the dehydroxylation in beidellite. The mass loss of structural OH units at high temperature shows that the clay is relatively stable at elevated temperatures [15]. The position of surfactant oxidation/decomposition temperature in the curves of the organo-beidellites is confirmed by comparison with the DTG curve of the pure TDTMA which shows a major intense peak at 267 °C with a mass loss of 95.0 % (see Fig. 1S in the supplementary material). The decomposition temperature and related % mass loss data from the thermogravimetric analysis in Fig. 2 are summarized in Table 1.

In some previous studies (under N_2), more than one peak for the desurfactant process can be observed, which indicates that the surfactant is present in different environments within the organo-clays [13, 16, 17]. In this study, the analysis atmosphere is composed of 20 % O_2 and 80 % Ar which is similar to that of air. Thus, the decomposition procedures of surfactant are very different. There are three steps for surfactant oxidation/decomposition. Compared with the decomposition temperature of pure TDTMA surfactant at about 267 °C, it is observed that the surfactant molecules within organo-beidellite are more thermal stable and the central peak position shifts slightly from 309 °C of 0.25CEC-TB to 274 °C of 1.25CEC-TB. The higher decomposition temperature may indicate that the mass loss is mainly from the exchanged TDTMA on the internal active sites of the clay.

An estimate of the real surfactant concentration (in units of CEC of the clay) of TDTMA onto beidellite was made for each organo-clay using TG data on the mass loss % of surfactant using a similar equation as created previously [16] which gives theoretical maximum and minimum values of the real adsorption amount of surfactant onto the clay.

$$\frac{(X \cdot 129 \cdot 10^{-5})(\text{mol})}{\text{g}} = \frac{[(m \cdot S\%) \div M](\text{mol})}{[m \cdot (100\% - S\%)](\text{g})} \tag{1}$$

$$X = \frac{m \cdot S\%}{(M - y) \cdot m \cdot (100\% - S\%) \cdot 129 \cdot 10^{-5}}$$
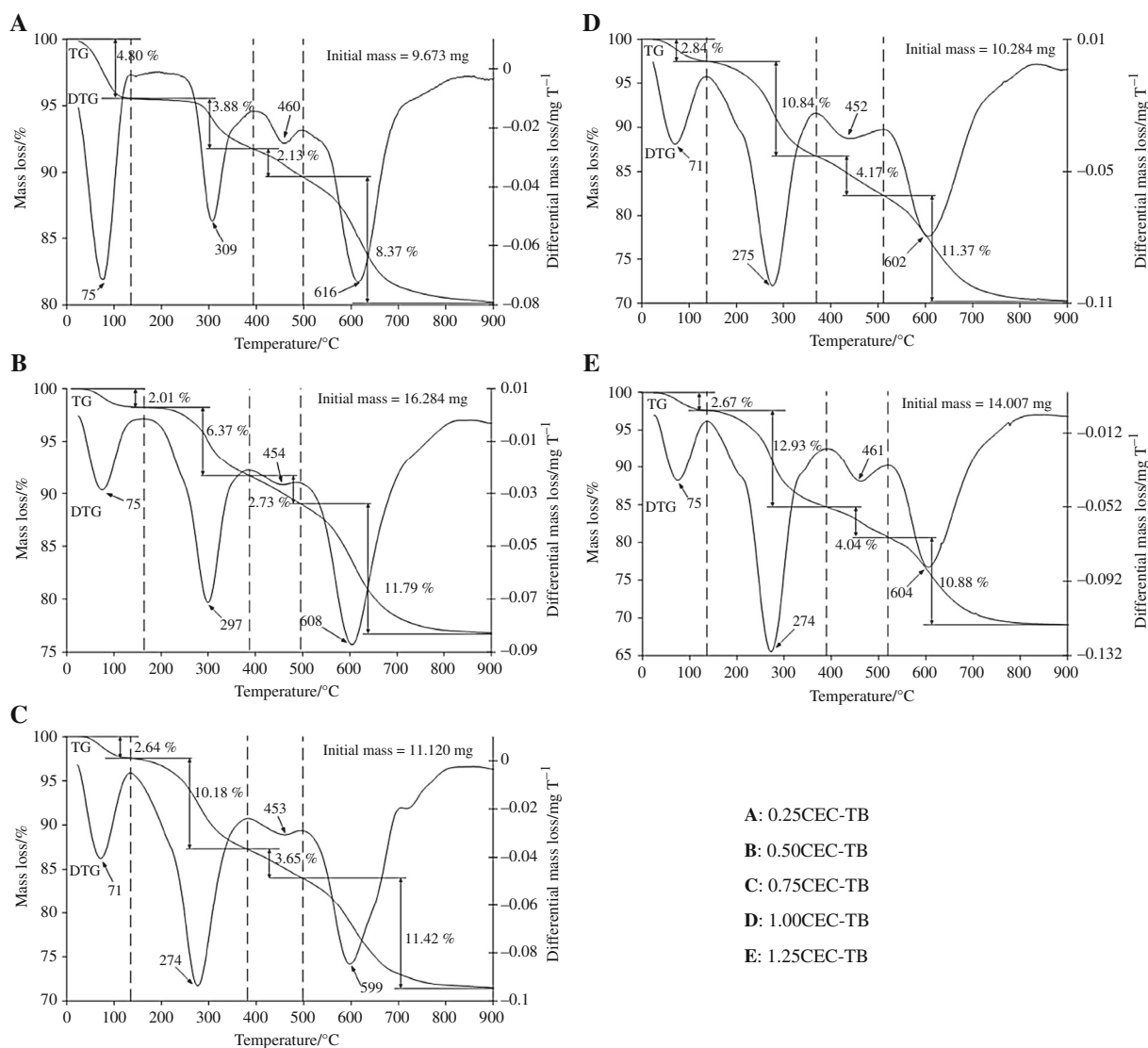$$= \frac{S\% \cdot 10^5}{129 \cdot (M - y) \cdot (100\% - S\%)} \tag{2}$$

Fig. 2 TG and DTG patterns of organo-beidellites

Table 1 Data from thermogravimetric analyses of organo-beidellites

Sample	Dehydration step		Surfactant oxidation/ decomposition step 1		Surfactant oxidation/ decomposition step 2		Surfactant oxidation/ decomposition step 3	
	% mass loss of sample	Temperature/°C	% mass loss of sample	Temperature/°C	% mass loss of sample	Temperature/°C	% mass loss of sample	Temperature/°C
0.25CEC-TB	4.80	75	3.88	309	2.13	460	8.37	616
0.50CEC-TB	2.01	75	6.37	297	2.73	454	11.79	608
0.75CEC-TB	2.64	71	10.18	274	3.65	453	11.42	599
1.00CEC-TB	2.84	71	10.84	275	4.17	452	11.37	602
1.25CEC-TB	2.67	75	12.93	274	4.04	461	10.88	604

Equation 1 is created based on the definition of cation exchange capacity. This equation can be converted to Eq. 2, where X is the loaded surfactant amount (in CEC); m is the total mass of organo-clay (g); M is the molecular mass of surfactant (g mol^{-1}); S% is the mass loss percentage of surfactant in organo-clay; y is 0 (if all the Br

Table 2 Real surfactant loading estimates of organo-beidellites

TDTMA added/CEC	Exchange value/CEC		Total mass loss % of surfactant in organo-clay
	With Br ion	Without Br ion	
0.25	0.387	0.508	14.38
0.50	0.609	0.798	20.89
0.75	0.778	1.02	25.25
1.00	0.826	1.08	26.38
1.25	0.890	1.17	27.85

ions remain) or 80 (no Br ion, the molecular weight of Br is 80), $y = 0$ or 80 is not possible to be reached, but it can be helpful in working out the range of X by calculating the theoretical maximum and minimum values. The CEC of beidellite at 129 meq/100 g and the molecular weight of TDTMA at 336.39 g mol^{-1} are used in the equation. The mass loss percentage of organo-clay is calculated based on the last three mass losses as described in Table 1. It should be noticed that the dehydroxylation mass loss in the fourth step is not deducted as it is much smaller than that of the surfactant. The results from these calculations are presented in Table 2.

Table 2 shows that there are some differences between the added amount and the loaded amount of surfactant in organo-beidellites. For example, in 0.25CEC-TB, the real adsorption amount is about 0.387–0.508 CEC of the clay which is more than the added amount. An increase in the added surfactant amount leads to an increase in the estimated real loading. For 0.50CEC-TB and 0.75CEC-TB, the loaded amounts of surfactants reached 0.609–0.798 CEC and 0.778–1.02 CEC, respectively. When the added amount of surfactant was increased further, the loaded amounts can reach 0.826–1.08 and 0.890–1.17 for 1.00CEC-TB and 1.25CEC-TB, respectively. Generally, the estimated real surfactant loading amount is higher than the added amount during the sample preparation procedure. When the added amount is close to or higher than one CEC, the calculated amount is very close to that of the added amount, and this may be due to the saturation of beidellite with surfactant. The amount of adsorbed water was gradually reduced from 4.80 to 2.67 %, indicating the increasing hydrophobicity of the organo-complex with increasing surfactant loadings.

Conclusions

TG and DTG have been used to characterize and compare the thermal decomposition behaviours of TDTMA-modified beidellites. There are mainly four mass losses of organo-beidellite, corresponding to dehydration surfactant oxidation, loss of OH units at the edge of clay layers/charcoal oxidation and dehydroxylation of the structural OH units/final oxidation of charcoal in the clay, respectively. TG/DTG is a powerful tool in estimating the loaded amount of surfactant. It is concluded that the developed equation can estimate the real surfactant loading into beidellite with accurate results. These findings are important on the quest from insights into the properties of organo-clays that may be useful for environmental remediation applications.

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