Journal of Thermal Analysis and Calorimetry, Vol. 91 (2008) 1, 261–265

THERMAL ANALYSIS OF SOME ORGANOCLAYS

M. Önal[*] *and Y. Sarıkaya*

Ankara University, Faculty of Science, Department of Chemistry, Tandoğan, 06100 Ankara, Turkey

Thermogravimetric (TG) and differential thermal analysis (DTA) curves of methyltributylammonium smectite (MTBAS), methyltrioctylammonium smectite (MTOAS), and di(hydrogenatedtallow)dimethylammonium smectite (DHTDMAS), and also corresponding sodium smectite (NaS) and tetraalkylammonium chlorides (TAAC) were determined. The TAACs was decomposed exactly by heating up to 500°C. The adsorbed water content of 8.0% in the pure NaS was decreased down to 0.2% depending on the size of the non-polar alkyl groups in the tetraalkylammonium cations (TAA^+). The thermal degradation of the organic partition nanophase formed between 2:1 layers of smectite occurs between 250–500°C. Activation energies (*E*) of the thermal degradations in the MTBAS, MTOAS and DHTDMAS are 13.4, 21.9, and 43.5 kJ mol^{-1}, respectively. The *E* value increases by increasing of the interlayer spacing along a curve depending on the size of the alkyl groups in the TAA^+.

Keywords: *activation energy, DTA, organosmectite, smectite, tetraalkylammonium cations, TG, thermal degradation*

Introduction

Clays such as kaolin, illite, palygorskite and sepiolite are among the most important industrial raw materials [1–4]. Bentonites and their major clay mineral smectites have been widely used in many applications depending on their high adsorption, swelling, and cation exchange capacities [5–9]. Inorganic and organic pillared clays have been prepared based on the cation exchange ability of smectites [10, 11]. Organic pillared clays (organoclays) are prepared by replacing natural inorganic exchangeable cations (Na^{2+}, Ca^{2+}), located between 2:1 layers of smectite, by alkylammonium, alkyldiammonium, and tetraalkylammonium cations [12–16]. Organoclays have been used in the production of sorbents, paints, lubricants, cosmetics, paper, medicines, ink, grease, resin, nanocomposites, and various high-strength materials [17, 18]. Several studies have been realized about the sorption of organic contaminants such as oils, phenolic compounds, herbicides, insecticides, and fungicides on organoclays [19–27].

The thermal behavior of organoclays has a great importance because it plays a key role in the preparation of polymer-smectite nanocomposites [28–31]. The organoclay-based nanocomposites must have mechanical strength, heat resistance, and biodegradability as well as low gas permeability and flammability [32–35]. These properties depend heavily on the organoclays. Therefore, thermal analysis in combination with other techniques, have been used to understand the thermal stability of the organoclays [36–41]. Several thermal analysis methods have been used to understand the thermal behavior of natural and artificial materials [42–56]. The aim of this study was to investigate the effect of the type of tetraalkylammonium cations on the hydrophilic–hydrophobic character and on thermal stability of some organoclays, and also to get better knowledge of the smectite remained after escaping of the organic phase, by thermal analysis.

Experimental

A sodium-rich smectite (NaS) having cation exchange capacity of 1.08 mol kg^{-1} was used in this study. It was isolated by purification of a bentonite taken from Reşadiye (Tokat/Turkey) region [57]. Basal spacing, *d*(001), for the anhydrous and air dried NaS were 1.00, 1.24 nm, respectively. Three tetraalkylammonium chloride (TAAC) salts, used in this study, were methyltributylammonium chloride (MTBAC, Merck), methyltrioctylammonium chloride (MTOAC, Merck), di(hydrogenatedtallow)dimethylammonium chloride (DHTDMAC, Berol-Nobel). They were used as received. Chemical formulas of the $MTBA^+$, $MTOA^+$ and $DHTDMA^+$ cations are $[CH_3N(C_4H_9)_3]^+$, $[CH_3N(C_8H_{17})_3]^+$, and $[(CH_3)_2NC_{16}H_{33}C_{18}H_{37}]^+$, respectively. Their carbon (C) numbers are 13, 25 and 36, respectively. They were as the smallest, medium, and the largest TAA cations to prepare sorptive organosmectites. TAA cations having C number of 12 or less than 12 have been used to prepare adsorptive organosmectites but not sorptive ones.

---

[*] Author for correspondence: onal@science.ankara.edu.tr

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Three organosmectites were prepared by using the NaS and TAA cations equivalent to the CEC. The preparation procedures and some physicochemical properties were given in our previous studies, but not thermal behaviors [58]. The prepared organosmectites by using $MTBA^+$, $MTOA^+$ and $DHTDMA^+$ cations are labeled as MTBAS, MTOAS, and DHTDMAS, respectively. The molar mass of the $MTBA^+$, $MTOA^+$ and $DHTDMA^+$ are 200, 368 and 522 g mol^{-1} and $d(001)$ spacing of the corresponding organosmectites are 1.47, 2.29 and 3.18 nm, respectively [58].

Thermogravimetry (TG) and differential thermal analysis (DTA) curves of the air dried TAA cations, NaS, and organoclays were recorded using a Shimadzu Apparatus (DTG-60H). Approximately 20 mg of sample was placed in a platinum crucible on the pan of the microbalance and was heated in the range 25–1000°C using α-Al_2O_3 as an inert material. Analysis was performed under flowing nitrogen with the rate of 100 mL min^{-1} using heating rate of 10°C min^{-1}. Two repeated TG-DTA experiments were performed for each sample. It is not seen any considerable difference among them.

Results and discussion

Thermal characteristics of the neat tetraalkylammonium salts

The TG and DTA curves of the used TAA salts were examined, and those of the neat DHTDMAC as representative one is shown in Fig. 1 for the temperature range of 25–500°C. Three endothermic and one exothermic change are seen in the DTA curve. The first endothermic change without any considerable mass loss with a maximum rate at 76°C is attributed to the phase transition of DHTDMAC. The second endothermic change with a mass loss of 35% and a maximum rate at 210°C is due to the partial decomposition of the neat DHTDMAC. The third endothermic change with a mass loss of 62% and a maximum rate at 375°C indicates the evaporation of the solid products. The exothermic peaks between 400–450°C show the combustion of a small amount of charcoal (~3%) formed by the decomposition. It is observed that all organic materials used in this study were decomposed completely up to 500°C.

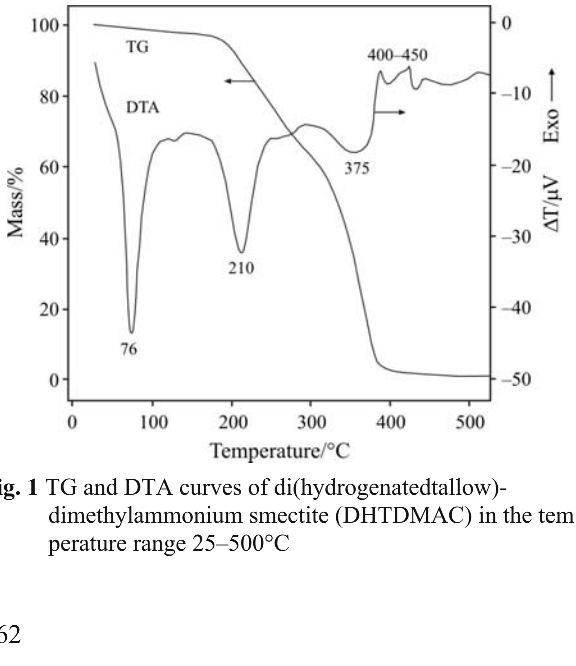

Fig. 1 TG and DTA curves of di(hydrogenatedtallow)-dimethylammonium smectite (DHTDMAC) in the temperature range 25–500°C

Thermal characteristics of the NaS

TG and DTA curves of the NaS are given Fig. 2 for the temperature range of 25–1000°C. The first and dominant endothermic mass loss of 8% between 25 and 200°C with a maximum rate at 160°C is due to the dehydration of interparticle water, adsorbed water, and interlayer water (*W*). The second endothermic mass loss of 6% between 550–700°C with a maximum rate at 650°C is originated from the dehydroxylation of the NaS. The exothermic change without mass loss and with a maximum rate at 920°C shows the recrystallization of the NaS. The total mass loss and the solid residue by heating up to 1000°C is 14 and 86%, respectively. The mass ratio of dehydroxylation water (*DW*) and the solid residue (*RE*) must be constant for a smectite. This ratio for the used NaS is calculated as DW/RE=6/86=0.0698. This ratio does not change in the case of the different organosmectites.

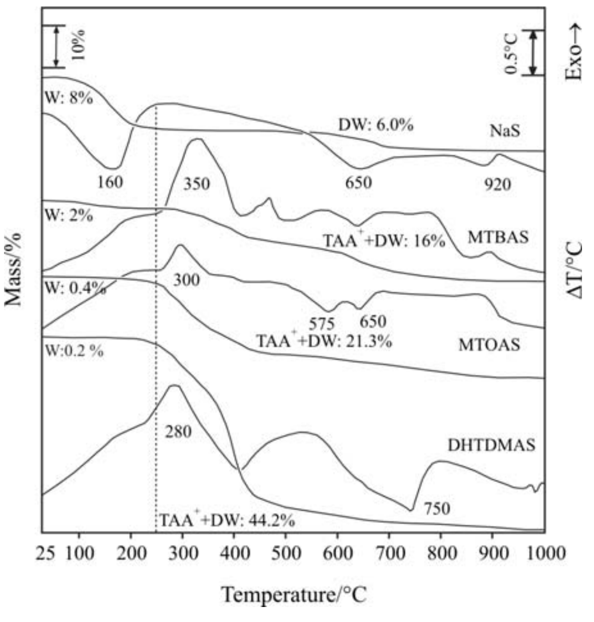

Fig. 2 TG and DTA curves of sodium smectite and organosmectites in the temperature range 25–1000°C (*W* – adsorbed water, *DW* – dehydroxylation water, TAA^+ – tetraalkylammonium cation)

Thermal characteristics of the organosmectites

TG and DTA of the MTBAS, MTOAS and DHTDMAS are shown in Fig. 2 for the temperature range of 25–1000°C. Thermal changes in the organosmectites may be divided into three steps. Dehydration of the water (*W*) occurs in the first step between 25–250°C. The intercalated TAA cations are degradated and besides small inorganic and organic molecules, as well as charcoal are formed in the second step between 250–500°C. Besides the dehydroxylation of the NaS, the combustion of the charcoal occurs in the third step between 500–1000°C. The differentiation of the mass losses originated from the dehydroxylation (*DW*) of the NaS and decomposition of the TAA cations are almost impossible from the TG curves. The total mass losses from the TAA cations and *DW* are given in Fig. 2. Furthermore, recrystallization of the NaS without any mass loss occurs between 900–1000°C in the third step. These changes are not exactly seen in the DTA curves.

Hydrophilic-hydrophobic character of the organosmectites

The water content (*W*) of the NaS decreases greatly from 8.0 to 0.2% by the formation of the organosmectites. This shows that the replacement of natural inorganic cations by TAA cations via ion exchange converts the smectite surface from hydrophilic to hydrophobic in character. Furthermore, the *W* decreases from 2.0 to 0.2% depending on the size of the TAA cations, as seen in Fig. 2. The variation of the *W*% with the molar mass (M^+) of the TAA cations is given in Fig. 3. Organophilic partition nanophase formed interlayers of smectite that interact strongly with organic vapors and compounds dissolved in water. This interaction and sorption capacity of organosmectites having large non-polar alkylgroups is greater than those of the natural smectites and intercalated smectites having small non-polar alkylgroups. It is well known that basal spacing, *d*(001), of organosmectites increase also depending on the size of the TAA cations. The variation of *d*(001) spacing with the molar mass of the TAA cations gives a straight line, as seen in Fig. 3.

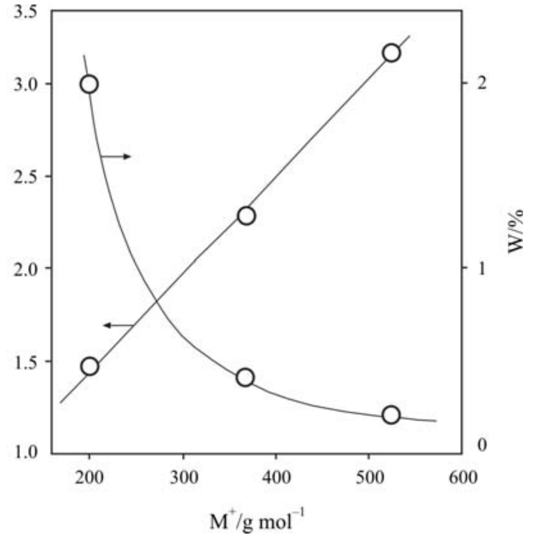

Fig. 3 The variation of basal spacing, *d*(001), and water content (*W*) of the organosmectites with the molar mass (M^+) of the tetraalkylammonium cation

Thermal degradation kinetics

Several methods have been used to evaluate kinetic parameters of solid-state reactions involving mass loss by thermogravimetry [32, 47, 59, 60]. The organic partition nanophase formed interlayers of the NaS degradates between 250–500°C as seen in Fig. 2. This degradation can be assumed approximately as first order reaction such as, solid (1)→solid (2)+gas. The activation energy (*E*) for such reaction can be calculated from the Coats and Redfern equation as follows [45, 61, 62].

$$\ln\{[-\ln(1-\alpha)]/T^2\}= -(E/RT)+\ln[(AR/\beta E)(1-2RT/E)] \quad (1)$$

where α is the mass fraction of the degradation calculated from TG data, *T* is the temperature (K), *R* is the universal gas constant, *A* is the frequency factor, and $\beta=dT/dt=10\ \mathrm{K\ s^{-1}}$ is the heating rate. The second term in this equation is nearly constant. The Coats–Redfern straight lines for the degradation of the organic partition nanophases formed in the organosmectites are given in Fig. 4. The activation energies for the

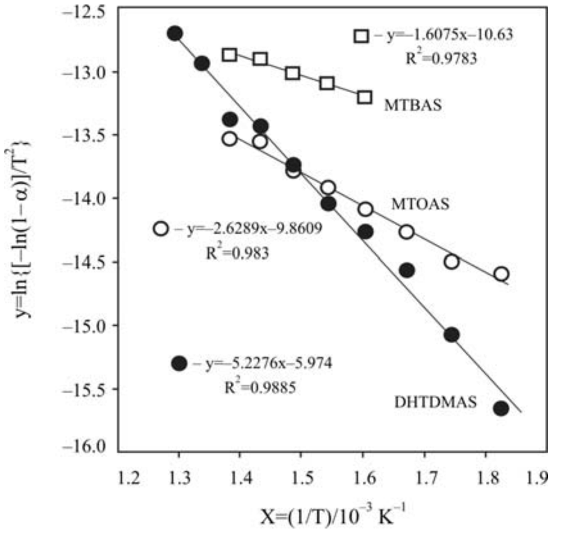

Fig. 4 The Coats and Redfern straight lines for degradation of interlayer organic partition nanophases formed in the prepared organosmectites in the temperature range 250–500°C

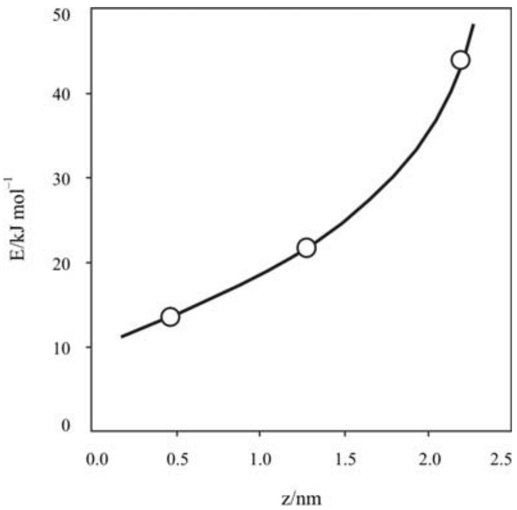

Fig. 5 The variation of the degradation activation energy (*E*) with the interlayer spacing (*z*) of the organosmectites

nanophases within MTBAS, MTOAS and DHTDMAS were calculated from the slopes of these straight lines as 13365, 21857 and 43462 J mol^{-1}, respectively. The thickness (*z*) of these partition nanophases were calculated from the difference of *d*(001)-values for the organosmectites and anhydrous NaS [58]. The variation of the activation energies *vs.* the nanophase thickness is given in Fig. 5. Activation energy increases by increasing of the nanophase thickness along a curve.

Conclusions

Tetraalkylammonium chlorides used in this study are decomposed exactly by heating up to 500°C. The increase in smectite surface from hydrophilic to hydrophobic depends on the size of non-polar alkylgroups in the tetraalkylammonium cations. The basal spacing of smectite increases linearly by increasing of the molar mass of the tetraalkylammonium cations. The activation energy of thermal degradation for the organic partition nanophase formed by intercalation of tetraalkylammonium cations between 2:1 layers of smectite increases with the increasing of interlayer spacing along a curve. This indicates that the catalytic effect of the smectite surface on the thermal degradation of the nanophase decreased by increasing of the interlayer spacing.

Acknowledgements

The authors thank the Scientific and Technical Research Council of Turkey (TÜBİTAK) for supporting this study under the project No: TBAG-2363 (103T138).

References

1 R. E. Grim, Clay Mineralogy, 2nd Ed., McGraw-Hill, New York 1968.
2 H. H. Murray, Appl. Clay Sci., 5 (1991) 379.
3 H. H. Murray, Clay Miner., 34 (1999) 39.
4 H. H. Murray, Appl. Clay Sci., 17 (2000) 207.
5 R. E. Grim and N. Güven, Bentonites, Geology, Mineralogy, Properties and Uses. Development in Sedimentology, Vol. 24, Elsevier, Amsterdam 1978.
6 L. H. Mollins, D. I. Stewart and T. W. Cousens, Clay Miner., 31 (1996) 243.
7 G. E. Christidis, Appl. Clay Sci., 13 (1998) 79.
8 P. F. Luckham and S. Rossi, Adv. Colloid Interface, 82 (1999) 43.
9 P. Komadel, Clay Miner., 38 (2003) 127.
10 J. M. Adams, Appl. Clay Sci., 2 (1987) 309.
11 L. P. Meier, R. Nueesch and F. T. Madsen, J. Colloid Interface Sci., 238 (2001) 24.
12 J. W. Jordan, J. Phys. Chem., 53 (1949) 294.
13 J. W. Jordan, B. J. Hook and C. M. Finlayson, J. Phys. Chem., 54 (1950) 1196.
14 G. Lagaly, Philos. Trans. R. Soc. London, A 311 (1984) 315.
15 R. M. Barrer, Clays Clay Miner., 37 (1989) 385.
16 P. G. Slade and W. P. Gates, Appl. Clay Sci., 25 (2004) 93.
17 M. M. Mortland, Adv. Agron., 22 (1970) 75.
18 S. M. Koh and E. J. Je, Miner. Ind., 14 (2001) 48.
19 M. M. Mortland, S. Shaobai and S. A. Boyd, Clays Clay Miner., 34 (1986) 581.
20 T. S. Sheriff, C. J. Sollars, D. Montgomery and R. Perry, Env. Techn. Lett., 8 (1987) 501.
21 S. A. Boyd, J. Lee and M. M. Mortland, Nature, 333 (1988a) 345.
22 S. A. Boyd, M. M. Mortland and C. T. Chiou, Soil Sci. Soc. Am. J., 52 (1988b) 652.
23 S. A. Boyd, S. Shaobai, J. Lee and M. M. Mortland, Clays Clay Miner., 36 (1988c) 125.
24 J. Lee, M. M. Mortland, C. T. Chiou, D. E. Kile and S. A. Boyd, Clays Clay Miner., 38 (1990) 113.
25 J. A. Smith and P. R. Jaffe, Water Air Soil Poll., 72 (1994) 205.
26 M. J. Carrizosa, W. C. Koskinen, M. C. Hermosin and J. Cornejo, Soil Sci. Soc. Am. J., 67 (2003) 511.
27 M. O. Adebajo, R. L. Frost, J. T. Kloprogge and O. Carmody, J. Porous Mater. 10 (2003) 159.
28 V. Hlavatý and A. Oya, J. Thermal Anal., 46 (1996) 521.
29 V. Hlavatý and V. Š. Fajnor, J. Therm. Anal. Cal., 67 (2002) 113.
30 E. Horváth, J. Kristóf, R. L. Frost, Á. Rédey, V. Vágvölgyi and T. Cseh, J. Therm. Anal. Cal., 71 (2003) 707.
31 S. Yariv, Appl. Clay Sci., 24 (2004) 225.
32 K. P. Pramoda, T. Liu, Z. Liu, C. He and H-J. Sue, Polym. Degrad. Stab., 81 (2003) 47.
33 S. S. Ray and M. Okamoto, Prog. Polym. Sci., 28 (2003) 1539.
34 C. I. Park, M. H. Kim and O. O. Park, Polymer, 45 (2004) 1267.
35 H. Krump, A. S. Luyt and I. Hudee, Mater. Lett., 60 (2006) 2877.

36 Y. Xi, Z. Ding, H. He and R. L. Frost, J. Colloid Interface Sci., 277 (2004) 116.
37 S. Yariv and I. Lapides, J. Therm. Anal. Cal., 80 (2005) 11.
38 Y. Xi, W. Martens, H. He and R. L. Frost, J. Therm. Anal. Cal., 81 (2005) 91.
39 M. M. G. Ramos Vianna, J. Dweck, V. F. J. Kozievitch, F. R. Valenzuela-Diaz and P. M. Büchler, J. Therm. Anal. Cal., 82 (2005) 595.
40 S. M. Koh, M. S. Song and T. Takagi, Clay Miner., 40 (2005) 213.
41 H. He, Z. Ding, J. Zhu, P. Yuan, Y. Xi, D. Yang and R. L. Frost, Clays Clay Miner., 53 (2005) 287.
42 Z. Malek, V. Balek, D. Garfinkel-Shweky and S. Yariv, J. Thermal Anal., 48 (1997) 83.
43 E. Mendelovici, J. Thermal Anal., 49 (1997) 1385.
44 A. Nasser, M. Gal, Z. Gerstl, U. Mingelgrin and S. Yariv, J. Thermal Anal., 50 (1997) 257.
45 Y. Sarıkaya, M. Önal, B. Baran and T. Alemdaroğlu, Clays Clay Miner., 48 (2000) 557.
46 M. V. Kök and W. Smykatz-Kloss, J. Therm. Anal. Cal., 64 (2001) 1271.
47 M. V. Kök, Energy Sources, 24 (2002) 899.
48 R. L. Frost, Z. Ding and H. D. Ruan, J. Therm. Anal. Cal., 71 (2003) 783.
49 R. L. Frost and M. L. Weier, Thermochim. Acta, 406 (2003) 221.
50 R. L. Frost, M. L. Weier, M. E. Clissold, P. A. Williams and J. T. Kloprogge, Thermochim. Acta, 407 (2003a) 1.
51 R. L. Frost, E. Horváth, E. Makó, J. Kristóf and A. Rédey, Thermochim. Acta, 408 (2003b) 103.
52 M. V. Kök, Energy Sources, 26 (2004) 145.
53 H. Noyan, M. Önal and Y. Sarıkaya, Clays Clay Miner., 54 (2006) 375.
54 N. Yener, M. Önal, G. Üstünışık and Y. Sarıkaya, J. Therm. Anal. Cal., 88 (2007) 813
55 H. Bayram, M. Önal, G. Üstünışık and Y. Sarıkaya, J. Therm. Anal. Cal., 89 (2007) 169.
56 M. Önal and Y. Sarıkaya, J. Therm. Anal. Cal., 90 (2007) 167.
57 M. Önal, Y. Sarıkaya, T. Alemdaroğlu and İ. Bozdoğan, Turk. J. Chem., 27 (2003) 683.
58 M. Önal and Y. Sarıkaya, Colloids Surf. A., 296 (2007) 216.
59 J. W. Stucki and D. L. Bish, Thermal Analysis in Clay Science, The Clay Minerals Society, Aurora, CO, USA, 1990.
60 F. Dabrowski, S. Bourbigot, R. Delobel and M. Le Bras, Eur. Polym. J., 36 (2000) 273.
61 A. W. Coats and J. P. Redfern, Nature, 201 (1964) 68.
62 Y. Sarıkaya, İ. Sevinç and M. Akınç, Powder Technol., 116 (2001) 109.

Received: March 4, 2007
Accepted: April 5, 2007
OnlineFirst: July 26, 2007

DOI: 10.1007/s10973-007-8319-x