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Structure of organo-clays--an X-ray diffraction and thermogravimetric analysis study

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Abstract

X-ray diffraction has been used to study the changes in the surface properties of a montmorillonitic clay through the changes in the basal spacings of montmorillonite (SWy-2) and surfactant-intercalated organo-clays.
Variation in the d-spacing was found to be a step-function of the surfactant concentration. High resolution thermogravimetric analysis (HRTG) was used to study the thermal decomposition surfactant modified SWy-2-MMTs modified with the surfactant octadecyltrimethylammonium bromide. High resolution thermogravimetry shows the decomposition takes place in 4 steps. A mass loss step is observed at room temperature and is attributed to dehydration of adsorption water. A second mass loss step is observed over the 87.9 to 135.5 °C temperature range and is also attributed to dehydration of water hydrating metal cations such as Na^+ . The third mass loss occurs from 178.9 to 384.5°C and is assigned to a loss of surfactant. The fourth mass loss step is ascribed to the loss of OH units through dehydroxylation over the 556.01 to 636.35°C temperature range.

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Keywords: montmorillonite, dehydration, dehydroxylation, organo-clay, X-ray diffraction, high-resolution thermogravimetric analysis

1. Introduction

Smectites are widely used in a range of applications because of their high cation exchange capacity, swelling capacity, high surface area and resulting strong adsorption/absorption capacities (1-4). In expanding clays, the most common dioctahedral smectite is montmorillonite, which has two silica-oxygen tetrahedral sheets sandwiching an aluminium or magnesium octahedral sheet, where an aluminium or magnesium ion is octahedrally coordinated to six oxygens or hydroxyls. Because of substitution of silicon by aluminium in the tetrahedral layers or similar substitution of aluminium ion by magnesium ion, montmorillonite layers are negatively charged. Thus, cations like sodium, potassium and calcium are attracted to the mineral surface to neutralize the negative layer charges. Because of the hydration of inorganic cations on the exchange sites, the clay mineral surface is hydrophilic in nature, which make natural clays ineffective sorbents for adsorbing organic compounds (5-7). Organo-montmorillonites are synthesized by grafting cationic surfactants such as quaternary ammonium compounds into the interlayer space (8-10). When using long-chain alkylammonium cations hydrophobic partition medium within the clay interlayer can form, and function analogously to a bulk organic phase. The intergallery distance of d(001) plane of the clay which has not been organically modified, is relatively small, and the intergallery environment is hydrophilic. Intercalation of organic surfactant between layers of clays can not only change the surface properties from hydrophilic to hydrophobic, but also greatly increase the basal spacing of the layers. At present, there are many applications of organo-clays using as sorbents in pollution prevention and environmental remediation such as treatment of spills, waste water, hazardous waste landfills etc. different areas. Some studies (11-14) have showed that replacing the inorganic exchange cations of clay minerals with organic cations can result in greatly enhanced capacity of the materials to remove organic contaminants.

This paper reports the changes in the structure of a montmorillonitic clay which

has been intercalated with a long chain organic surfactant. X-ray diffraction and high resolution thermogravimetric analyses are used to study the changes in the surfactant concentration dependent organo-clays. The objective of the research is the study of the change in structure of the organoclays with surfactant concentration.

2. Experimental

2.1. Materials

The montmorillonite used in this study was supplied by the Clay Minerals Society as source clay SWy-2-Na-Montmorillonite (Wyoming). This clay originates from the Newcastle formation, (cretaceous), County of Crook, State of Wyoming, USA. The cation exchange capacity (CEC) is 76.4 meq/100g (according to the specification of its producer). The surfactant used in this study is octadecyltrimethylammonium bromide ($C_{21}H_{46}NBr$, FW: 392.52) from Sigma-Aldrich.

2.2. Preparation

The syntheses of surfactant-clay hybrids were undertaken by the following procedure: 4g of SWy-2-Na-montmorillonite was first dispersed in 400ml of deionized water then under stirring with a Heidolph magnetic stirrer at about 600rmp for about 16h. A pre-dissolved stoiciometric amount of octadecyltrimethylammonium (ODTMA) bromide solution was slowly added to the clay suspension at 60 °C. The concentrations of $ODTMA^+$ used are 0.2 CEC (Cation Exchange Capacity), 0.4 CEC, 0.6CEC, 0.8CEC, 1.0CEC, 1.5CEC, 2.0CEC, 3.0CEC and 4.0 CEC of the SWy-2-montmorillonite, respectively. The reaction mixtures were stirred for 30 min at 60 °C using a Branson Ultrasonics model 250 sonifier with an output of 40 mW. All organo-clay products were washed free of bromide anions, dried at room temperature and ground in an agate mortar, stored in a vacuum desiccator for about 7 days.

2.3. Characterization methods

2.3.1. Methods for X-ray diffraction

The SWy-2-montmorillonite and surfactant montmorillonite hybrids were pressed in stainless steel sample holders. X-ray diffraction (XRD) patterns were recorded using CuKα radiation (n = 1.5418Å) on a Philips PANalytical X' Pert PRO diffractometer operating at 40 kV and 40 mA between 3 and 15° (2θ) at a step size of 0.0167°.

2.3.2. Methods for TG

Differential thermal and thermogravimetric analyses of the surfactant montmorillonite hybrids were obtained using a TA® instruments Inc. Q500 high resolution TGA operating at high resolution ramp 10 °C/min resolution 6.0 °C from room temperature to 1000 °C in a high purity flowing nitrogen atmosphere (80 cm^3/min). Approximately 50mg of sample was heated in an open platinum crucible. No preparation was required other than grinding the sample up finely. For SWy-2-montmorillonite, the TGA instrument was coupled to a Balzers (Pfeiffer) mass spectrometer for gas analysis (for other surfactant montmorillonite hybrids and pure surfactant, mass spectrometer is disconnected, because organic gases may block the capillary of the mass spectrometer). Only selected gases were analyzed.

3. Results and discussion

3.1. X-ray diffraction

With the cation exchange of the sodium ion for the cationic surfactant expansion of the montmorillonitic clay layers occurs. This expansion is readily measure by X-ray diffraction. Figure 1 shows the XRD patterns of SWy-2-Na-montmorillonite and surfactant montmorillonite hybrids at different surfactant concentrations. Figure 2 clearly shows the increase in the basal spacing from 11.6864 Å to > 20 Å for OMMT-1.5, OMMT-2.0, OMMT-3.0 and OMMT-4.0 as concentration of the surfactant used is increased. The graph also shows that for OMMT-0.2, the basal spacing is slightly larger than that of 0.4 CEC hybrid OMMT-

0.4, (14.6783 Å and 14.6515 Å respectively). It is possible that for OMMT-0.2, the concentration of surfactant is quite low that there are still large amount of exchangeable Na^+ which can adsorb water because of their high hydration energy, it makes the basal spacing larger than that of OMMT-0.4. When 1.5 CEC of surfactant is used, the basal spacing reaches a maximum. From 1.5 CEC to 4.0 CEC, the increase in the basal spacings only increases slightly. In addition, from the configuration structure point of view, for OMMT-0.2 (0.2CEC) and OMMT-0.4 (0.4CEC), the d values are 14.6783 and 14.6515 Å respectively. This implies a lateral-monolayer arrangement of $ODTMA^+$ in the interlayer space of montmorillonite. For OMMT-0.6 (0.6CEC) and OMMT-0.8 (0.8CEC), the d values are 17.7072 Å and 17.9448 Å respectively, which reflect lateral-bilayer arrangement. From OMMT-1.5 (1.5CEC) to OMMT-4.0 (4.0CEC), the d basal spacings reach over 20 Å, which reflects a pseudotrimolecular layer arrangement. As for OMMT-1.0 (1.0CEC), the d value is 19.7214 Å, it means the arrangement of surfactant is between lateral-bilayer and pseudotrimolecular layer structure.

3.2. High resolution thermogravimetric analysis (HRTG)

The high resolution thermogravimetric analysis (HRTG) for the SWy-montmorillonite, surfactant and organo-clays are shown in Figure 3 (derivative weight %/°C versus temperature). The temperatures of the evolved gas MS mass gain of SWy-2-MMT are shown in Figure 4. The result of the analyses of the mass loss and temperature of the mass loss are reported in Table 1. Several mass loss steps are observed. A mass loss step is observed from room temperature and is attributed to the mass loss due to dehydration/dehydroxylation (adsorption water). A second mass loss step is observed over the 87.9 to 135.5 °C temperature range and is also attributed to dehydration of water adsorbed by metal cations such as Na^+, Ca^{2+} etc. For 0.2CEC and 0.4CEC-MMT, the total weight losses of adsorption water are 8.189 % and 4.273 % respectively. This proves that 0.2 CEC-MMT contains more water than 0.4 CEC-MMT. This explains why the basal spacing of 0.2 CEC-MMT is bigger than that of 0.4 CEC-MMT. The third mass loss occurs from 178.9 to 384.5 °C. For OMMT-0.6, 0.8, 1.0, 1.5, 2.0, 3.0, and 4.0, there is more than one peak.

By comparing the TG patterns of pure surfactant with that of SWy-2-MMT, it

is concluded that the loss of surfactant occurs at 250°C for pure $C_{21}H_{46}NBr$. The fourth mass loss step is ascribed to the loss of dehydroxylation of the structural OH units of the montmorillonite over the 556.0 to 636.3 °C temperature range. Generally speaking, the second dehydration/dehydroxylation step is observed for montmorillonite and some of the low concentration of surfactant modified clays (SWy-2-MMT, 0.2CEC-0.8CEC surfactant modified clays). The first % mass loss for dehydration of adsorption water varies from 1.787% up to 6.664%. The experimental % mass loss during the second dehydration/dehydroxylation of adsorption water varies from 0.2189% up to 2.204%. The experimental % mass loss during de-surfactant varied from 5.146% (0.2CEC-MMT) to 47.47% (4.0CEC-MMT), 100% (pure surfactant). In addition, the peak maxima of the DTG de-surfactant procedure of organo-clays are different. For 0.2 CEC and 0.4 CEC-MMT, there is only one peak. The centre of the peaks are 384.51°C and 380°C respectively. For 0.6 CEC and 0.8 CEC-MMT, there are two peaks for each sample (281.17/381.16°C for 0.6CEC-MMT and 283.03/378.83°C for 0.8CEC-MMT). From 1.0CEC-MMT to 4.0CEC-MMT, there are three peaks for every sample. As a conclusion, it shows that when the concentration of the organo-clay is relatively low (for example 0.2CEC and 0.4CEC), there is only one peak (the peak position is around 380°C), with the increase of the concentration of surfactant, a new peak appears (centre position is about 280°C) and the intensity of this peak increases with the increase of surfactant used, if the concentration of surfactant increases further, the third peak will appear (it varies from 178.9 to 233.0 °C) and the intensity of this peak also increases with the increase of the surfactant used.

When the concentration of the surfactant is relatively low, the organic cations ion exchange with the Na^+ ions and mainly adhere to surface sites via electrostatic interactions. With the increase of the concentration of surfactant, some of surfactant molecules attach to the surface of montmorillonite. This results in the appearance of the second peak. If the concentration increases further, the concentration of the surfactant exceeds the CEC of clay. Surfactant molecules then adhere to the surface adsorbed surfatant cations by van der Waals forces.

The properties of these organic cations is very similar to that of pure surfactant. So the third peak appears at about 178.9 to 233.0 °C which is close to 200.4 °C—the

temperature of the pure surfactant. In addition, with the increase of the concentration of the surfactant, the temperature of the third peak decreases gradually (becomes closer to that of the pure surfactant). In addition, there was a considerable difference between temperature of pure surfactant and surfactant in the organo-clays. This may be due to some surfactants attached strongly to the montmorillonite that causes an increase the decomposition temperature.

4. Conclusions

The basal spacing obtained from X-ray diffraction give details of arrangement of surfactant in the organo-clays. For OMMT-0.2 and OMMT-0.4, there is a lateral-monolayer arrangement of $ODTMA^+$ in the interlayer space of montmorillonite. For OMMT-0.6 and OMMT-0.8, the surfactant takes a lateral-bilayer arrangement. From OMMT-1.5 to OMMT-4.0, the d basal spacings reach > 20 Å, which reflects a pseudotrimolecular layer arrangement. As for OMMT-1.0 (1.0CEC), the arrangement of surfactant is between lateral-bilayer and pseudotrimolecular layer structure. The utilization of HRTGA allows one to distinguish between different concentrations of surfactant modified clays and to provide more information of their configuration and structural changes in the organo-clays. It shows that there are mainly about four mass loss steps ascribed to (a) water-desorption (b) dehydration (c) de-surfactant (d) dehydroxylation of clay OH units. In addition, three different environments of surfactant in organo-clays have been discussed.

Acknowledgements

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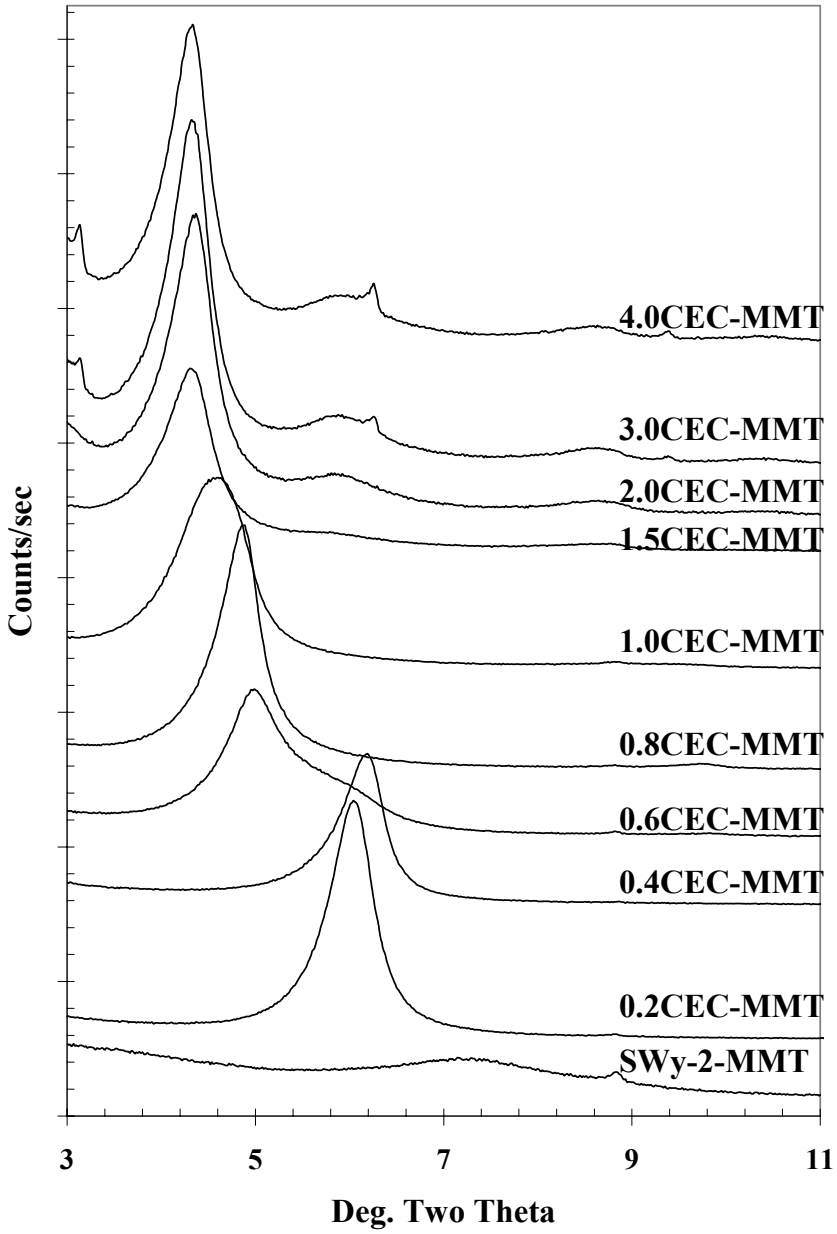
4.0CEC-MMT
3.0CEC-MMT
2.0CEC-MMT
1.5CEC-MMT
1.0CEC-MMT
0.8CEC-MMT
0.6CEC-MMT
0.4CEC-MMT
0.2CEC-MMT
SWy-2-MMT
Counts/sec
3
5
7
9
11
Deg. Two Theta

Figure 1

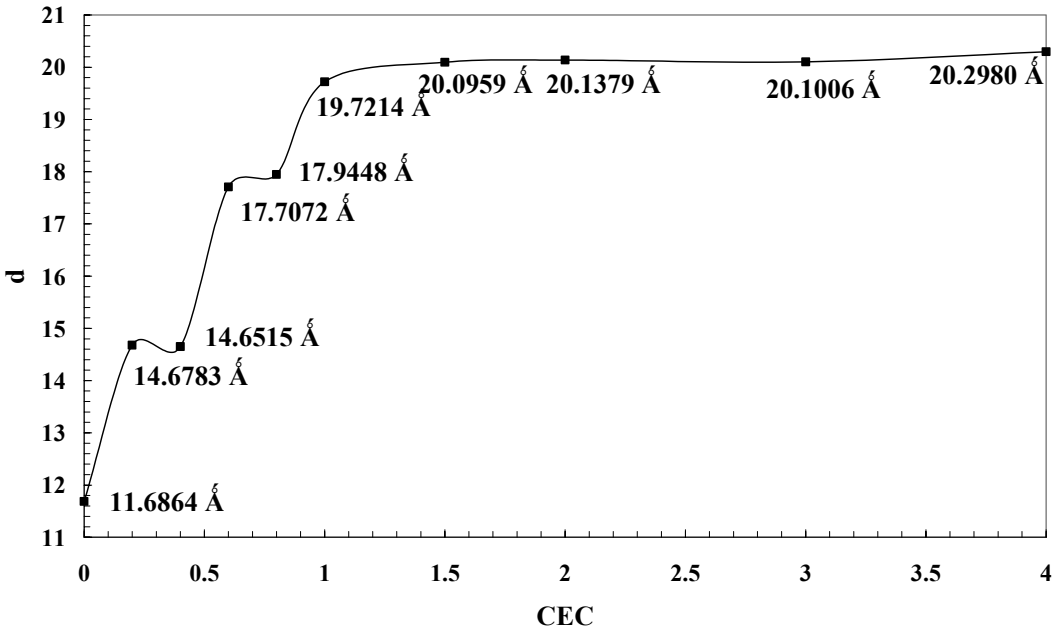
21
20
19
18
17
16
15
14
13
12
11
d
0
0.5
1
1.5
2
2.5
3
3.5
4
CEC
11.6864 Å
14.6783 Å
14.6515 Å
17.7072 Å
17.9448 Å
19.7214 Å
20.0959 Å
20.1379 Å
20.1006 Å
20.2980 Å

Figure 2

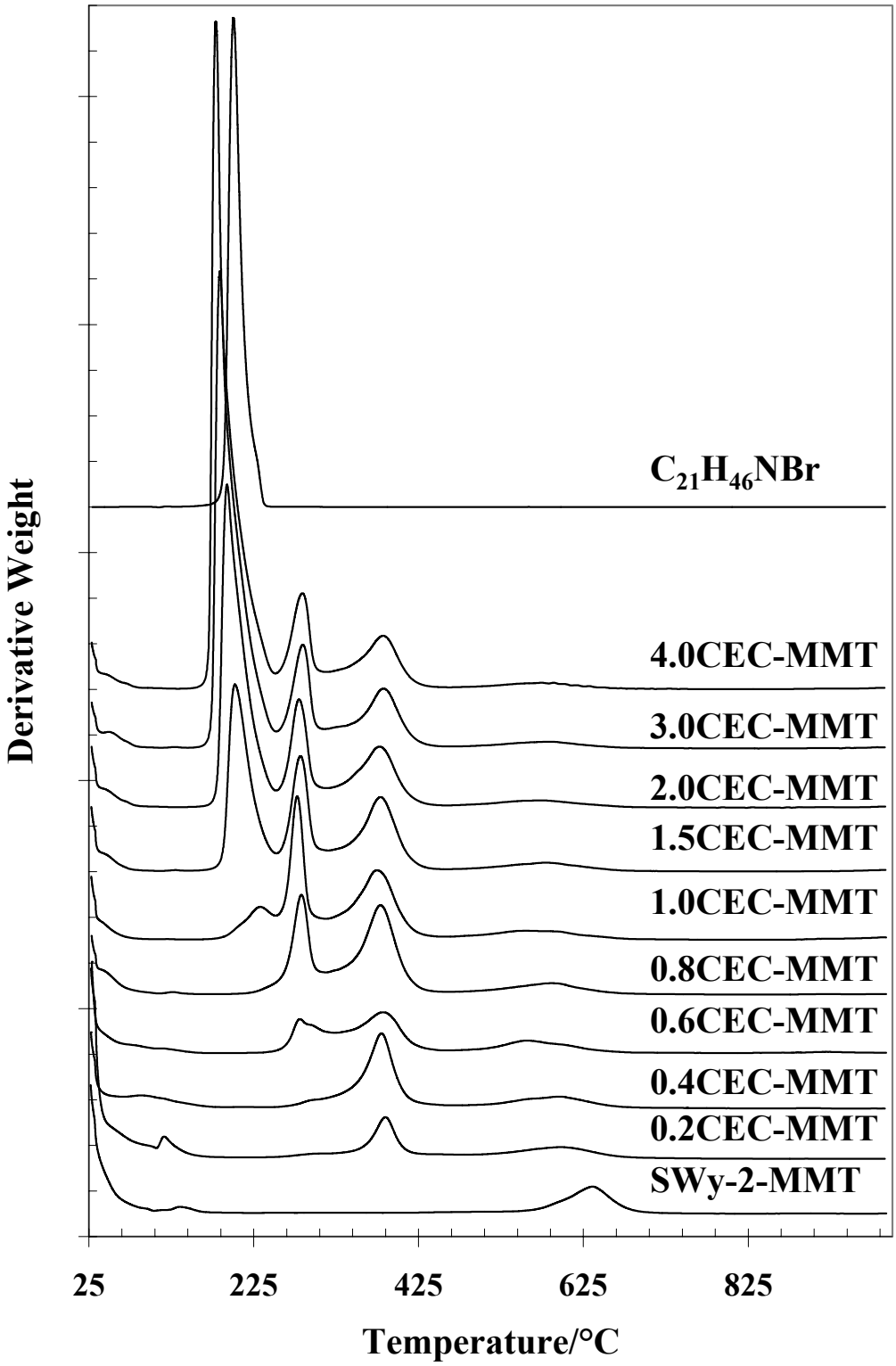
Derivative Weight
C21H46NBr
4.0CEC-MMT
3.0CEC-MMT
2.0CEC-MMT
1.5CEC-MMT
1.0CEC-MMT
0.8CEC-MMT
0.6CEC-MMT
0.4CEC-MMT
0.2CEC-MMT
SWy-2-MMT
25
225
425
625
825
Temperature/°C

Figure 3

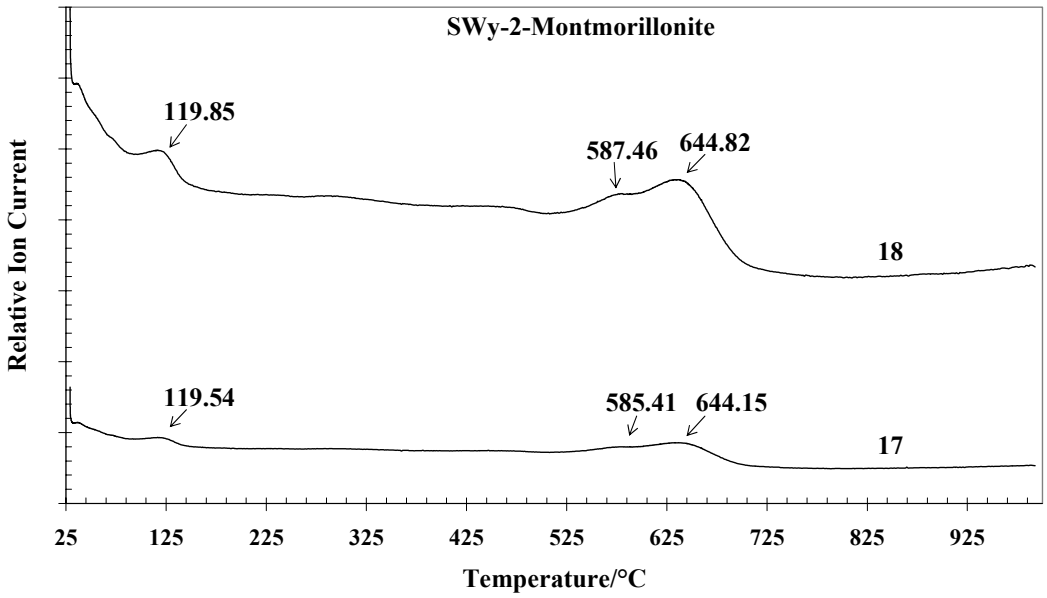
SWy-2-Montmorillonite
119.85
587.46
644.82
18
119.54
585.41
644.15
17
Relative Ion Current
25
125
225
325
425
525
625
725
825
925
Temperature/°C

Figure 4

Table 1 Results of the HRTG of SWy-MMT, surfactant and surfactant MMT hybrids.

Samples	% mass loss (step 1)	Temp (°C)	% mass loss (step 2)	Temp (°C)	% mass loss (step 3)	Temp (°C)	% mass loss (step 4)	Temp (°C)
	De-hydration/hydroxylation (adsorption water)		De-hydration/hydroxylation (water adsorbed by metal cations)		De-surfactant		De-hydroxylation (the structural OH units)	
Swy-2-MMT	4.369		1.065	135.53			4.917	636.35
0.2CEC-MMT	6.664		1.525	116.37	5.146	384.51	3.543	598.16
0.4CEC-MMT	2.069		2.204	87.91	9.099	380	3.686	598.2
0.6CEC-MMT	3.114		0.5015	113.61	10.16	281.17/381.16	4.539	556.01
0.8CEC-MMT	2.475		0.2189	126.99	17.78	283.03/378.83	3.417	589.13
1.0CEC-MMT	1.953				20.31	233.05/277.74/374.75	3.593	562.04
1.5CEC-MMT	2.131				29.70	202.26/281.87/379	2.899	579.36
2.0CEC-MMT	2.201				36.31	192.49/279.97/377.78	2.547	573.25
3.0CEC-MMT	1.958				44.25	183.99/284.68/382.58	2.224	582.98
4.0CEC-MMT	1.787				47.47	178.97/283.96/381.83	2.130	589.33
$C_{21}H_{46}NBr$					100	200.44		