Thermal analysis and application of organoclays for water purification

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Introduction
In recent years, organoclays have become widely used in many industrial applications, and particularly they have been applied as adsorbents for water purification (de Paiva et al., 2008; Zhou et al., 2008; Park et al., 2011). When the organoclays are enhanced by intercalation of cationic surfactant molecules, the surface properties are altered from hydrophilic to highly hydrophobic. These changes facilitate their industrial applications which are strongly dependent on the structural properties of organoclays (Koh and Dixon, 2001; Zeng et al., 2004; Cui et al., 2007). Thus a better understanding of the configuration and structural change in the organoclays by thermogravimetric analysis (TG) is essential. It has been proven that the TG is very useful for the study of complex minerals, modified minerals, and nanomaterials (Laachachi et al., 2005; Palmer et al., 2011; Park et al., in press, 2011). Therefore, the current investigation involves the thermal stability of a montmorillonite intercalated with two types of cationic surfactants: dodecyltrimethylammonium bromide (DDTMA) and didodecyldimethylammonium bromide (DDDMA) using TG. The modification of montmorillonite results in an increase in the interlayer or basal spacing and enhances the environmental and industrial application of the obtained organoclay.

Results and Discussion
Thermal stability of montmorillonite and organoclays, and packing arrangement of intercalated surfactant molecules within the organoclays have been investigated at an elevated temperature. The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of montmorillonite and organoclays intercalated with the mono- and di- alkyl cationic surfactants, DDTMA and DDDMA are displayed in Figures 1, 2 and 3.
Fig. 1. TG and DTG of montmorillonite.

(a) 

(b) 

(c) 

(d) 

Fig 2. TG and DTG curves of 0.5 CEC-DDTMA (a), 1.0 CEC-DDTMA (b), 2.0 CEC-DDTMA (c), and the surfactant (DDTMA) (d).
Fig 3. TG and DTG curves of 0.5 CEC-DDDMA (a), 1.0 CEC-DDDMA (b), 2.0 CEC-DDDMA (c), and the surfactant (DDDMA) (d).

From the results, four thermal decomposition steps are proposed: the first two steps involved the dehydration of surface adsorbed and interstitial water molecules near metal cations such as Na$^+$ or Ca$^{2+}$ (~200 °C). The third step related to the decomposition of the surfactant. It is noted that the decomposition temperature of surfactant intercalated in organoclays is higher than that of pure surfactant (at 194 °C for DDTMA and at 164 and 219 °C for DDDMA). The result indicates that the surfactant molecules bonded to the MMT siloxane layer requires more heat, and hence, a higher temperature was used to remove the surfactant molecules bonded on the clay surfaces (Zhou et al., 2007). With increasing surfactant loading, from 0.25 CEC to 2.0 CEC, the number of mass loss peaks increased. These results suggest that the loading of surfactant strongly influenced the number of mass loss steps present and further shows that the surfactants are intercalated in different within the organoclays. The last step involved the dehydroxylation of structural OH units in the clay at high temperature. The obtained thermal stabilities of montmorillonite and montmorillonite intercalated with two types of cationic surfactants will enhance the understanding of the surface properties and
structural changes in organoclays and have further potential implications of the industrial and environmental use of the organoclays.

References


