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Synthesis of organoclays: A critical review and some unresolved issues

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ABSTRACT

The synthesis of organoclays (OC) by intercalation of quaternary ammonium cation (QAC) into expanding clay minerals, notably montmorillonite (Mt), has attracted a great deal of attention during the past two decades. The OC have also found applications in the manufacture of clay polymer nanocomposites (CPN) and environmental remediation. Despite the wealth of information that exists on the formation and properties of OC, some problems remain to be resolved. The present contribution is an attempt at clarifying two outstanding issues, based on the literature and experimental data obtained by the authors over the past years. The first issue concerns the relationship between the cation exchange capacity (CEC) of the Mt and the basal spacing of the OC which, in turn, is dependent on the concentration and the nature of the added QAC. At a concentration less than 1 CEC, organo-Mt (OMt) formed using the QAC with a short alkyl chain length with $n_c < 16$ (e.g., dodecyl trimethylammonium) gives basal spacings of 1.4–1.6 nm that are essentially independent of the CEC. However, for long-chain QAC with $n_c \geq 16$ (e.g., hexadecyl trimethylammonium), the basal spacing varies with the QAC concentration. For Mt with a CEC of 80–90 meq/100 g, the basal spacing of the OC increases gradually with the CEC and shows a sudden (stepwise) increase to 3.2–3.8 nm at a QAC concentration of 1.5 CEC and to 3.5–4.0 nm at a concentration of 2.0 CEC. The second issue pertains to the "locking" effect in QAC- and silane-modified pillared interlayered clays (PILC) and Mt. For silylated Mt, the "locking" effect results from the covalent bonding of silane to two adjacent layers within a single clay mineral particle. The same mechanism can operate in silane-grafted PILC but in this case, the "locking" effect may primarily be ascribed to the pillaring of adjacent basal surfaces by metal hydr(oxides).

1. Introduction

The term 'organoclays' denotes a family of hydrophobic materials, obtained by modifying clays and clay minerals with various organic compounds through intercalation process and surface grafting (Bergaya and Lagaly, 2001; Bergaya et al., 2011a; He et al., 2013; Lagaly et al., 2013; Paiva et al., 2008). Organoclays (OC) have found important practical applications, notably as adsorbents of organic pollutants (Bergaya and Lagaly, 2013; Stockmeyer, 1991; Theng et al., 2008; Zhu and Chen, 2000; Zhu et al., 2000) and as components in the formation of clay polymer nanocomposites (Bergaya et al., 2011a, 2013a; Ray and Okamoto, 2003; Theng, 2012). A large volume of literature has accumulated over the past two decades on various aspects of OC research, including i) synthesis and characterization (Lagaly, 1981; Lagaly et al., 2013; Zhu et al., 2003); ii) surface properties and stability (He et al., 2005; Theng et al., 2008; Zhu et al., 2008); iii) production of clay-based nanocomposites (Bergaya et al., 2013a; Lambert and Bergaya, 2013; Ray and Okamoto, 2003; Theng, 2012); and iv) synthesis of novel materials using the OC as precursors (Bergaya and Lagaly, 2011; Ishii et al., 2005).

A more recent development that has attracted much interest is the preparation of QAC-modified pillared interlayered clay minerals (Annabi-Bergaya, 2008; Tahani et al., 1999a). Possessing both hydrophilic and hydrophobic surfaces as well as a large porosity and surface area, these materials are potentially useful as adsorbents of volatile organic compounds (VOC) as well as of organic and inorganic contaminants in waste water (Bouberka et al., 2009; Ouellet-Plamondon et al., 2012; Zhu et al., 2007, 2009a).

Among the smectite groups, montmorillonite (Mt) has held the limelight in the preparation of OC because of its moderate charge density and cation exchange capacity (CEC), interlayer swelling ability, and propensity for intercalating simple and polymeric organic compounds (Bergaya et al., 2011b, 2012; Lagaly and Dékany, 2013; Murray, 2000; Swartzen-Allen and Matijevic, 1974; Theng, 1974, 2012), not to mention its availability and low cost. At the same time, quaternary ammonium halides bearing long alkyl chains have been widely used for modifying clay minerals because of the ease with which the QAC can exchange the inorganic compensator exchangeable cation in the interlayer space of Mt.

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Notwithstanding the wealth of information that exists on the synthesis of OC, several points remain to be clarified. These include i) the relationship between the CEC and the OC structure; ii) the stability of OC under different chemical and physical conditions; iii) the relationship between QAC dosage and adsorption capacity otherwise on QAC/CEC ratio; and iv) the "locking" effect in the QAC-modified pillared interlayered clays and silane-grafted clay minerals.

With the aim to provide a helpful guide to the future synthesis and application of OC, points i) and iv) are considered based on the information from the open literature, and measurements carried out over the past 15 years.

2. Relationship between the CEC of the smectite and the basal spacing of the OC

Smectites are 2:1 silicates in which the unit layer consists of an octahedral sheet sandwiched between two opposing tetrahedral sheets. Because of isomorphous substitution, that is, the replacement of structural cations by other cations of lower valency (e.g., Al^{3+} by Mg^{2+}, or Mg^{2+} by Li^+, in the octahedral sheet; and Si^{4+} by Al^{3+} in the tetrahedral sheet), the layer structure acquires a negative charge which is balanced by (inorganic) cations in the interlayer space (Brigatti et al., 2013). These compensator cations are exchangeable, and the sum of their charges represents the CEC conventionally expressed in milliequivalents per 100 g clay (meq/100 g). The SI unit for CEC, $cmol_{(+)}/kg$, is numerically identical (Bergaya et al., 2013b). By the same token, the magnitude of the CEC determines the amount of QAC that can enter the interlayer space by a cation exchange.

A number of studies have been conducted regarding the effects of alkyl chain length and chain number, the nature of the polar head and the concentration (added QAC/CEC ratio), of QAC on the structure, and the properties of the resultant OC (He et al., 2010; Lagaly, 1981; Mandalia and Bergaya, 2006; Vaia et al., 1994; Xie et al., 2002). Generally, the basal spacing of OC increases with the alkyl chain length (expressed as number of carbon atoms, n_c) and the concentration of the QAC. The intercalated QAC may adopt different configurations, ranging from a flat monolayer to a paraffin bilayer through a lateral bilayer and a paraffin monolayer (Lagaly, 1981; Zhu et al., 2003). When the concentration exceeds the CEC, the QAC intercalates as an ion pair; that is, accompanied by the corresponding (halide) anion (Janek and Lagaly, 2003; Klapyta et al., 2001; Lee and Kim, 2002; Tahani et al., 1999b). At the same time, the QAC may enter the interparticle pore space, causing a decrease in the thermal stability of the resultant OC (He et al., 2005). Occupancy of interparticle pores by the QAC also leads to a dramatic decline in pore volume and specific surface area (SSA), while the propensity of the OC for adsorbing organic contaminants in solution is greatly increased (He et al., 2006a). These observations provide an insight into the microstructural properties of OC that are highly important and relevant to their industrial applications.

A survey of the literature shows that the OC prepared using the same QAC, and under similar experimental conditions, are often structurally different (He et al., 2006a, 2006b; Lagaly, 1981; Lee and Kim, 2002; Xi et al., 2005; Zidelkheir and Abdelgoad, 2008). This finding suggests that not only the structural properties of OC are dependent of the characteristics of the QAC used but also are strongly influenced by the nature of the clay mineral component. The chemical composition of a given clay mineral is also known to vary from one deposit to another because of the differences in parent (primary) rock chemistry and weathering conditions. Compositional variations are reflected by the magnitude of the CEC, arising from isomorphous substitution in the layer structure.

The literature (e.g., He et al., 2010; Lagaly, 1981) indicates that the QAC with a relatively short alkyl chain ($n_c < 14$) are intercalated as a lateral (flat) layer rather than in a paraffin arrangement over a wide range of QAC concentrations. Although the basal spacing of the resultant OC strongly depends on the size of the QAC used, its magnitude is slightly affected by the CEC of the clay mineral component.

Ma (2010) synthesized three series of OC using Mt with different CEC (72.4, 88.8, and 106.5 meq/100 g, the corresponding montmorillonites were denoted as Mt-1, Mt-2 and Mt-3, respectively.) and varying concentrations of dodecyl trimethylammonium (DTMA), ranging from 0.2 to 4.0 CEC. (1 CEC denotes a concentration equivalent to the CEC of the mineral). For Mt-1 with the lower CEC (72.4 meq/100 g), the OC prepared at a DTMA concentration of <1 CEC gave a basal spacing of 1.4 nm while the materials formed at DTMA concentrations of 1–4 CEC gave a basal spacing of 1.8 nm (Fig. 1). Interestingly, the OC prepared from the two other Mts (Mt-2 and Mt-3) with higher CEC values (88.8 meq/100 g and 106.5 meq/100 g, respectively) at DTMA concentrations of <1.5 CEC, showed X-ray diffraction (XRD) patterns almost identical to those prepared from Mt-1. However, when the initial DTMA concentration exceeded at 1.5 CEC, the XRD patterns of the OC showed a strong, broad reflection at 1.9 nm and a weak peak at 4.0 nm. Thus, large basal spacings can be obtained with the QAC having a relatively short alkyl chain ($n_c < 16$) when the QAC/CEC ratio is sufficiently high. These results obtained by Ma (2010) clearly indicate that the CEC of the Mt component has a marked effect on the basal spacing of the resultant OC although this factor, as reported below, is not as important as the chain length of the QAC.

The interlayer structural evolution of OC for the QAC with a long alkyl chain ($n_c \geq 16$) is very different from that prepared using the QAC with a relatively short alkyl chain ($n_c < 16$). Table 1 lists the basal spacings (d_{001}) of organo-Mt (OMt) prepared from the Mt with different CEC and varying concentrations (0.5–2.0 CEC) of hexadecyl trimethylammonium bromide (HDTMAB), collected from the literature. The relationship of the CEC of Mt and the basal spacing of the resultant OC (Table 1) is plotted in Fig. 2. In agreement with the previous findings (Li and Ishida, 2003), the basal spacing of OMt increases as the concentration of the added QAC is raised.

The OMt prepared using a HDTMAB concentration of 0.5 CEC, gives very similar basal spacings (1.4–1.6 nm) (Fig. 2). Since the amount of added HDTMAB, in this instance, is less than that of the CEC of the Mt, practically all of the $HDTMA^+$ are intercalated as expected through a cation exchange mechanism, giving rise to a lateral (monolayer) arrangement in the interlayer space (Lagaly, 1981; Zhu et al., 2003). An exception was reported by Carrizosa et al. (2004) who measured a basal spacing of 2.2 nm for an OC prepared from Arizona Mt with a CEC of 120 meq/100 g, which is the largest value reported for a Mt. In this case, the $HDTMA^+$ apparently adopted paraffin (instead of a lateral layer) arrangement, probably because the absolute $HDTMA^+$ concentration was appreciably larger than that used in preparing OC from the Mt with usually lower CEC.

From Fig. 2, we can find that the CEC of Mt has a slight effect on the basal spacing of the resultant OC when the concentration of added $HDTMA^+$ is less than 1 CEC. On the other hand, when the concentration equals the CEC of Mt, the basal spacing of the formed OC gradually increases as the CEC increases from 44 to 138 meq/100 g. Thus, the larger the CEC of the Mt component, the greater is the amount of intercalated $HDTMA^+$. The observed increase in basal spacings of the OMt may be explained in terms of the intercalation of $HDTMA^+$ as a lateral bilayer ($d_{001} \sim 1.8$ nm), a pseudotrilayer ($d_{001} \sim 2.0$ nm), or a paraffin monolayer ($d_{001} \sim 2.2$ nm) (Choy et al., 1997; Lagaly, 1981; Lambert and Bergaya, 2013; Theng et al., 2008; Zhu et al., 2003).

The XRD patterns of HDTMAB-modified clay minerals formed at a HDTMAB concentration of 1.5 CEC and 2.0 CEC show a sudden steep increase in basal spacing for Mt with a CEC of >80 meq/100 g, from 2.0–2.5 nm to 3.2–3.8 nm at 1.5 CEC and to 3.5–4.0 nm at 2.0 CEC (Fig. 2). Clearly, the CEC of the Mt has a profound effect on the basal spacing of the OC prepared at HDTMAB concentrations of 1.5 to 2.0 CEC. On the other hand, Jović-Jovičić et al. (2010) and Mojović et al. (2011) reported that the basal spacings of the OMt prepared at a HDTMAB concentration of 2.0 CEC were similar to the values obtained at 1.0 CEC. However, it should be noticed that these authors did not show the low-angle ($2\theta = 1$–$3°$) part of the XRD patterns. As such,
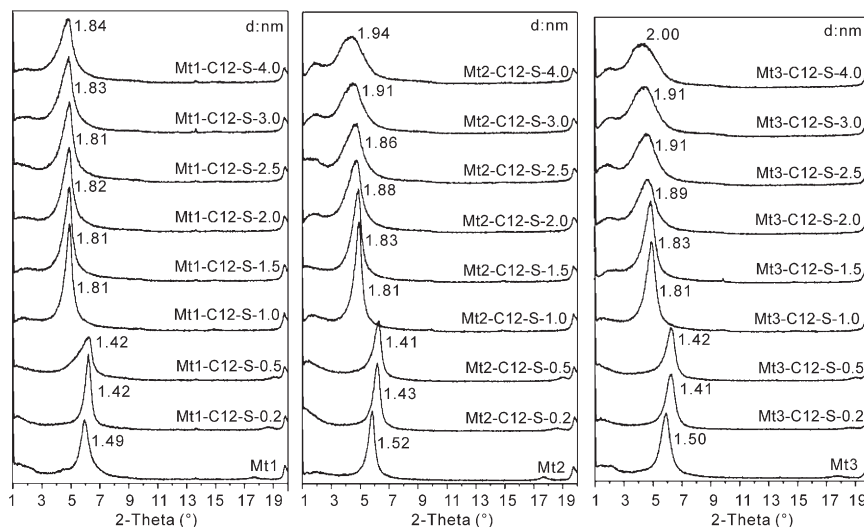
Fig. 1. X-ray diffraction (XRD) patterns of OC prepared from Ca^{2+}-Mt having different CEC (Mt1: 72.4 meq/100 g, Mt2: 88.8 meq/100 g and Mt3:106.5 meq/100 g, respectively) and at varying concentrations of dodecyl trimethylammonium surfactant (C_{12}-S), ranging from 0.2 to 4.0 CEC. Numbers alongside peaks denote basal spacings (in nanometers) (Ma, 2010).

Table 1
Basal spacings of OMt prepared at different concentrations of hexadecyl trimethylammonium bromide (HDTMAB) in solution.

CEC[a] (meq/100 g)	d_{001} (nm)				References
	0.5 CEC	1.0 CEC	1.5 CEC	2.0 CEC[b]	
44	1.4	1.8	n.d.	n.d.	(Carrizosa et al., 2004)
45	n.d.	n.d.	2.51	n.d.	(Koswojo et al., 2010)
52	1.44	1.84	n.d.	n.d.	(Marsal et al., 2009)
54	n.d.	2.1	n.d.	n.d.	(Xin et al., 2011)
57	1.67	2.02	n.d.	n.d.	(Li et al., 2009)
57.9	1.48	1.98	n.d.	n.d.	(He et al., 2006b)
63	1.52	2.0	n.d.	2.0	(Mojović et al., 2011)
63.9	1.41	2.00	n.d.	n.d.	(Lee et al., 2002)
69	1.86	1.90	n.d.	2.02	(Fatimah and Huda, 2013)
70	1.44	1.97	n.d.	n.d.	(Feng et al., 2009)
76	1.7	1.8	n.d.	n.d.	(Carrizosa et al., 2004)
76	n.d.	n.d.	n.d.	3.9	(Ma, 2010)
78	n.d.	2.06	n.d.	n.d.	(Jović-Jovičić et al., 2010)
80	1.46	1.99	2.15	2.39	(Gammoudi et al., 2012)
80	1.69	2.15	n.d.	n.d.	(Sánchez-Camazano and Sánchez-Martín, 1994)
80	n.d.	2.06	n.d.	n.d.	(Vianna et al., 2005)
82	1.68	1.90	n.d.	3.65	(Volzone et al., 2006)
87	n.d.	1.81	n.d.	n.d.	(Zhao and Vance, 1998)
88.8	n.d.	n.d.	n.d.	3.7	(Ma, 2010)
90.8	1.48	1.95	2.23	3.61	(He et al., 2006a)
90.8	1.48	n.d.	2.71	n.d.	(Zhou et al., 2007)
90.8	1.44	2.25	n.d.	2.95	(Chen, 2008)
91	1.58	1.80	n.d.	n.d.	(Yílmaz and Yapar, 2004)
92	n.d.	1.80	n.d.	n.d.	(Bergaya et al., 2005)
92	1.45	1.82	3.26	4.05	(Mahadevaiah et al., 2011)
93	n.d.	2.03	n.d.	n.d.	(Dentel et al., 1998)
97	n.d.	2.1	n.d.	n.d.	(Zaghouane-Boudiaf and Boutahala, 2011)
98	1.76	2.57	n.d.	3.94	(Volzone et al., 2006)
100	n.d.	2.55	3.84	n.d.	(Wang et al., 2012)
100	n.d.	1.89	n.d.	n.d.	(Yan et al., 2007)
104	1.51	1.95	n.d.	n.d.	(Lee et al., 2004)
106	1.46	2.01	n.d.	n.d.	(Zhou et al., 2010)
106.5	1.7	2.3	3.4	3.9	(He et al., 2010)
108	n.d.	2.39	n.d.	n.d.	(Zhu et al., 2009b)
110.6	1.43	2.21	3.47	3.73	Results of our experiments
120	2.2	2.3	n.d.	n.d.	(Carrizosa et al., 2004)
130	n.d.	2.2	n.d.	n.d.	(Zhao and Vance, 1998)
138	n.d.	2.45	n.d.	n.d.	(Liu et al., 2012)

n.d. = not determined.
[a] Cation exchange capacity (CEC) of the untreated (parent) montmorillonite (Mt).
[b] Surfactant concentration in solution: 1 CEC denotes a concentration equivalent to the CEC of montmorillonite.

the d value (2.00 nm) reported by the authors could be (002) reflection instead of (001) reflection of OMt.

When the concentration of the added HDTMAB exceeds 2.5 CEC, the OMt apparently reach a "saturated" state, giving a (maximum) basal spacing of ~4.0 nm. He et al. (2010) have found similar results for the three series of OC obtained from the Mt with different CEC (72.4 meq/100 g, 88.8 meq/100 g and 106.5 meq/100 g) using varying concentrations (0.2–4.0 CEC) of HDTMAB. The three OMts gave closely similar XRD patterns with basal spacings of 4.1 nm, indicative of "saturation" when HDTMAB penetrated into the interlayer space and interparticle pores of the Mt through both cation exchange and physical adsorption (He et al., 2006a).

3. Locking effect in the QAC- and silane-modified pillared interlayered clays (PILC) and Mt

There are some drawbacks in the application of OC in that, part of the interlayer QAC may leach into the surrounding solution, and enter the interparticle pore space, making the materials less effective in adsorbing contaminant species. By comparison, the QAC-modified and silane-grafted pillared interlayered clays (PILC) are potentially superior adsorbents because they have a relatively large pore volume and SSA (Heylen et al., 1995; Khalaf et al., 1997; Michot and Pinnavaia, 1992; Qin et al., 2010).
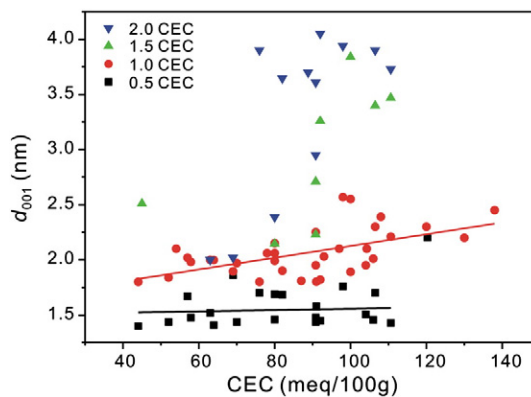

Fig. 2. Relationship between the CEC of Mt and the basal spacing (d_{001}) of the resultant OC formed at different concentrations (0.5–2.0 CEC) of hexadecyl trimethylammonium bromide (HDTMAB).

A number of studies have demonstrated that the QAC-modified PILC, also named 'inorgano-organo clays', have an appreciably higher capacity for adsorbing organic contaminants than their unmodified counterparts (Bouberka et al., 2005, 2009; Tahani et al., 1999a; Zhu et al., 2009a). These materials are also effective in taking up both the organic and inorganic contaminants simultaneously (Zhu et al., 2009a).

Inorgano–organo clays may be synthesized by three different methods: (1) intercalation of the metal hydr(oxide) polycation into swelling clay minerals (to form PILC), followed by the QAC of choice to modify the PILC (Bergaya et al., 2005); (2) mixing the polycation and QAC, and intercalating the mixture into the clay mineral; and (3) intercalation of the QAC (to form an OC), followed by that of the polycation (Bouberka et al., 2009; Zhu et al., 2009b).

The basal spacings of the inorgano–organo clay minerals, obtained using the methods 2 and 3, are dependent on the concentration of the added QAC. This finding is consistent with the intercalated QAC and polycation being attached to the interlayer surfaces of the clay mineral by electrostatic forces. The material obtained using method 1, however, is structurally different from that prepared by methods 2 and 3. Ma et al. (2014) used all three synthesis methods to obtain the several series of inorgano–organo Mt. A "locking" effect was observed for Mt, pillared with hydroxy-aluminum (Al_{13}) cations, and calcined at 300–500 °C, before being modified by the intercalation of HDTMAB. Since the basal spacings of the inorgano–organo Mt were similar to those of the initial (unmodified) Al_{13}-pillared Mt, they suggested that contiguous layers of individual PILC particles were locked by Al_{13}-pillars, resulting in a loss of interlayer expansion (Fig. 3). By controlling the interlayer height (separation), the locking effect may be used to vary the packing density of the intercalated QAC by changing the QAC concentration in solution. The pore volume and SSA of inorgano–organo clays may similarly be adjusted.

Zhu et al. (2007) were the first to synthesize silylated PILC by pillaring Mt with Al_{13} cations and then silylating the PILC with alkylchlorosilanes (Fig. 4). The thermal stability of the silylated products was generally superior to that of the QAC-modified PILC. Water adsorption tests further showed that the hydrophobicity of silane-grafted PILC was greatly enhanced in comparison with the corresponding (ungrafted) PILC.

The factors affecting the structure and surface properties of Al_{13}-pillared Mt, grafted with 3-aminopropyltriethoxysilane (APTES) have been investigated by Qin et al. (2010). These factors included the pretreatment (calcination) temperature of the PILC, the temperature

of grafting, and the characteristics of the solvents used. Prior calcination of Al_{13}-Mt at high temperatures (e.g., 500 °C) led to a decrease in the amount of grafted silane, while both the pore volume and SSA of the product increased. This finding was ascribed to the partial loss of hydroxyl groups in the structure of intercalated Al_{13} cations where silylation took place. These authors also found that non-polar solvents (e.g., cyclohexane) were more favorable to silane grafting than that to polar solvents (e.g., ethanol). Unlike its unmodified counterpart, the silane-grafted PILC could effectively remove Orange II from water.

Qin et al. (2010) further noted that the basal spacings of PILC were almost identical to those of the silane-grafted counterparts, suggesting the "locking" of adjacent silicate layers by the interlayer pillars similar to what happened in the QAC-modified PILC. On the other hand, for uncalcined Al_{13}-Mt, the configuration and size of the silane used had a marked effect on the basal spacing of the grafted products (Zhu et al., 2007). This finding indicates the absence of a "locking" effect as Ma et al. (2014) have suggested for the QAC-modified Al_{13}-Mt. It would therefore appear that the "locking" effect is due to the formation of interlayer pillars during, and as a result of, calcination rather than to the intercalation of Al_{13} polycations.

In this connection, it should be pointed out that the "locking" effect in silane-grafted PILC may also arise from the simultaneous condensation of silane (or silane oligomers), having more than two hydrolysable groups, with adjacent silicate layers. Such a process of locking has never been mentioned in reports about silane-grafted PILC although its occurrence has been proposed in the silane-grafted clay minerals (Herrera et al., 2004, 2005; Su et al., 2012).

He et al. (2013) have pointed out that both the interlayer and external basal surfaces, as well as the edge surface of expanding 2:1 layer silicates (smectites), are potentially available to silane grafting. As would be expected, a successful grafting of silane to external particle surfaces does not affect the basal spacing of smectites (Park et al., 2004). On the other hand, the intercalation of silane into the Mt causes a marked increase in the basal spacing of the grafted mineral (Piscitelli et al., 2010; Shen et al., 2007). There is a good evidence to indicate that the broken edges of clay mineral particles are the most reactive sites for the silane grafting (Daniel et al., 2008; He et al., 2014; Herrera et al., 2004, 2005).

The "locking" effect was proposed by Su et al. (2012) to account for the swelling behavior of the silylated Mt. These authors found that the basal spacing of Mt increased from 1.48 nm to 2.09 nm after grafting
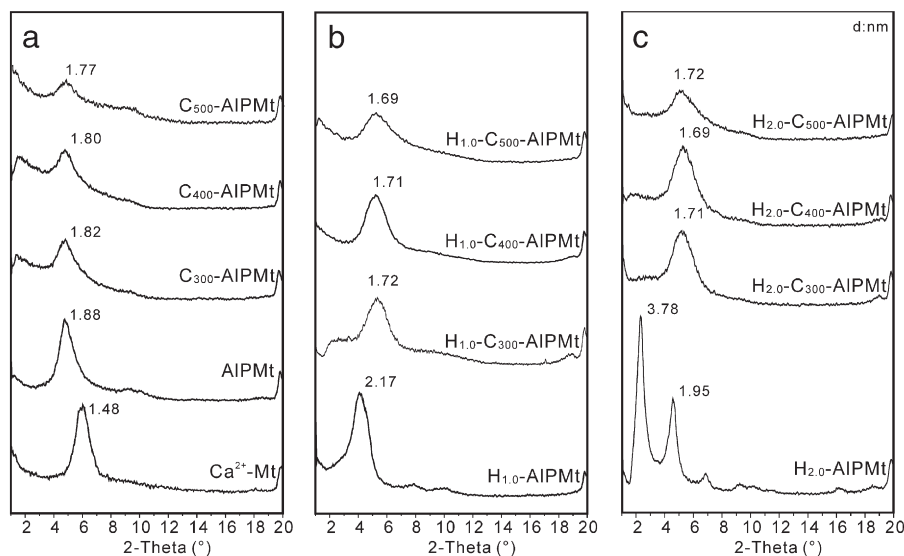

Fig. 3. (a), XRD patterns of Ca^{2+}-Mt and Al_{13}-pillared montmorillonite (AlPMt) before and after calcination at 300 °C (C_{300}), 400 °C (C_{400}), and 500 °C (C_{500}); (b), XRD patterns of AlPMt and its calcined derivatives after modification with the HDTMAB at a concentration of 1.0 CEC ($H_{1.0}$); (c), XRD patterns of AlPMt and its calcined derivatives after modification with the HDTMAB at a concentration of 2 CEC ($H_{2.0}$). Numbers over and alongside peaks denote basal spacings (in nanometers).
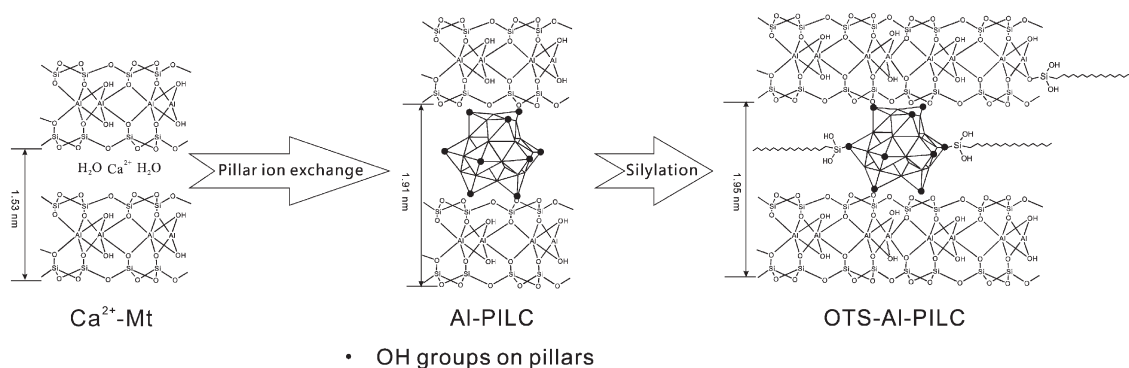
Fig. 4. Diagram showing the process of preparing octadecyltrichlorosilane (OTS) grafted PILC from Ca^{2+}-Mt. Al denotes Al_{13} polycation. (Zhu et al., 2007).

the mineral with 3-aminopropyltriethoxysilane (APTES), a trifunctional silylating agent. Further, the Q^2 signal attributed to Si located at the broken edge surface of the Mt particles was not detected, while the intensity of the Q^3 signal increased, following grafting. Here, Q^m (m = 0, 1, 2, 3, 4) refers to the polymerization state of the Si, i.e., Q^2 and Q^3 stand for Si linking to two and three other Si atoms via bridging oxygen atoms, respectively (He et al., 2003).

These observations were ascribed to the intercalation of silane molecules into the Mt. Interestingly, the basal spacing of the silylated products remained unchanged (~2.09 nm) following the intercalation of HDTMAB at a concentration of 2.0 CEC, while the basal spacing of HDTMAB-intercalated Mt reached 3.74 nm. In explanation, Su et al. (2012) suggested that the silane was grafted through the simultaneous condensation of molecule (or its oligomers) to the interlayer surfaces of Mt, locking successive layers within a particle.

The "locking" effect in PILC, arising from interlayer pillaring, has been recognized for a long time, whereas that induced by the covalent bonding of silane to adjacent clay mineral layers has only recently been described. Qin et al. (2010) have proposed that the interlayer pillars in the silane-grafted PILC provide the sites for the silane grafting. As already remarked on, it seems likely that a similar "locking" effect is also operative in the silane-grafted clay minerals.

4. Concluding comments and future outlook

The formation and properties of OC have been well documented. Nevertheless, some important issues pertaining to their syntheses remain unresolved. A survey of the literature indicates that the alkyl chain length and concentration of the added QAC (QAC/CEC ratio) have a marked effect on the basal spacing of OC, and hence on the arrangement of the intercalated QAC. Although for a given QAC size and concentration, the basal spacing of the corresponding OC is influenced by the CEC of the clay mineral (Mt) used, this relationship is not straight forward. The complex interdependence of the OC basal spacing, QAC size, QAC/CEC ratio, and CEC should be born in mind in the cost-effective preparation of OC for practical applications.

When the OC are used as adsorbents of dissolved pollutants, the intercalated QAC may leach into the surrounding solution, giving rise to secondary pollution. For this reason, one would advocate the use of organic compounds that are environmentally friendly and biodegradable, such as betaine, zwitterionic imidazoline, and amino acids. Measurements by Zhu et al. (2011) have indicated that the OC prepared with zwitterionic surfactants, having both positively and negatively charged groups as well as special functional groups, is effective in removing various pollutants from water. The OC containing biodegradable organic compounds would be expected to find wide applications in environmental engineering.

The stability of OC can be greatly improved by silylation through which the organic components are immobilized by a covalent bonding to the clay mineral surface. More importantly, some special functional

groups (e.g., $-NH_2$, $-SH$) can be incorporated into the silylated products in order to enhance the capacity of the OC for the selective adsorption of heavy metals. Recently, this family of novel OC has attracted great interest in terms of their potential applications in the synthesis of CPN and environmental remediation.

The positively charged metal hydr(oxide) species, notably Al_{13} polycations, intercalated into the Mt, have long been known to act as pillars, following calcination of the resultant Al_{13}-Mt, locking successive layers within a single clay mineral particle. A similar "locking" effect has recently been recognized in the silane-modified clay minerals when silane is covalently bonded to two adjacent clay mineral layers. In the case of silane-grafted PILC and clay minerals, however, there are some uncertainties regarding grafting mechanisms and sites. Molecular simulation and quantum calculation, under different experimental conditions, could open the way to resolving these problems at the atomic scale.

The "locking" effect may have a negative influence on the synthesis and application of clay-based nanocomposites. At the same time, its occurrence may be used to good effect in making novel materials with a well-defined interlayer separation or pore size distribution that can serve as the adsorbents and molecular sieves of environmental pollutants such as the VOC. Like CPN, the silylated clay minerals may well become versatile clay-based materials of wide practical applicability.

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