Review article

Silylation of clay mineral surfaces

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ABSTRACT

Silylation of clay mineral surfaces has attracted much attention because silylated products exhibit properties suitable for many applications in materials science and environmental engineering. Successful silylation strongly depends on the reactivity of clay mineral surfaces (e.g., density of surface hydroxyl), characteristics of silane (e.g., number of functional group and configuration of silane) and the reaction conditions (e.g., polarity of solvent and reaction temperature). For non-swelling clay minerals such as kaolinite, pre-intercalation with small polar molecules is an indispensable step in the silylation of interlayer surfaces. The temperature of the grafting reaction has a significant influence on silane intercalation, and the displacement of pre-intercalated molecules, as well as on the structure of the silylated products. On the other hand, silane is readily intercalated into swelling clay minerals such as montmorillonite. The broken edges of 2:1 type clay minerals are the most reactive sites for grafting. The polarity of the solvents used is another important factor controlling the extent of grafting, and the basal spacing of the silylated products. Grafting silane during the course of clay mineral synthesis (defined as in situ silylation in this review) has proved to be an efficient way of silylating clay mineral surfaces.

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1. Introduction

Surface modification of clay minerals has attracted much attention because the obtained products exhibit properties suitable for many applications in material science (Carrado, 2000; Herrera et al., 2004; LeBaron et al., 1999; Okada and Usuki, 2006; Ray and Okamoto, 2003) and environmental engineering (Guerra et al., 2012; He et al., 2006; Xu et al., 1997). Generally, two main methods were used in the modification of clay mineral surfaces, i.e., physical and chemical methods (Bergaya and Lagaly, 2001; Bergaya et al., 2006). Modifying clay minerals with various surfactants is the most widely used physical method to prepare inorganic/organic hybrid materials and accordingly clay mineral–polymer nanocomposites (CPN) (Ray and Okamoto, 2003). The obtained materials exhibit remarkable improvements in certain properties such as increased strength and heat resistance, decreased gas permeability and flammability (Ray and Okamoto, 2003). In this case, surfactants enter the interlayer spaces mainly by replacing the initial inorganic cations and electrostatic force is the main linkage between surfactant cations and clay mineral (Lagaly, 1981; Yariv, 2004). Two main problems will be encountered in their applications. A secondary pollution may be resulted from the leaching of the intercalated surfactant into the surrounding solutions when the organoclays are used as adsorbents (He et al., 2006). The weak electrostatic interaction leads to an obvious interface between hydrophilic clay mineral and hydrophobic organic matter, resulting

in a negative influence on the mechanical strength of CPN. Meanwhile, the edges of the organoclays still show hydrophilic, which will hinder the intercalation of bulky hydrophobic molecules and lead to an aggregation and segregation of clay mineral particles in the polymer matrix (Ray and Okamoto, 2003).

To solve the above-mentioned problems, great efforts have been made to build up novel methods during the last decade, to modify or functionalize clay mineral surfaces effectively and efficiently. Recently, silylation, also known as silane grafting, has proved to be an efficient way to silylate clay mineral surfaces (Avila et al., 2010; He et al., 2005). The covalent bonding between organic components and clay minerals enables a durable immobilization of the organic moieties in the silylated products (da Fonseca and Airoldi, 2003; LeBaron et al., 1999; Takahashi and Kuroda, 2011), and prevents their leaching into the surrounding solutions. Meanwhile, by introducing special functional groups in the organosilane agents used, the adsorption selectivity of the resultant materials to contaminants could be greatly improved (Bergaya et al., 2006; da Fonseca and Airoldi, 2001; da Fonseca et al., 2000a; de Mello Ferreira Guimarães et al., 2009; Guerra et al., 2009; Oh et al., 2007; Sayılkan et al., 2004). In the resultant CPN, organosilane is a key bridge between clay minerals and polymer matrix, which provides silanol to condensate with M−OH on the clay mineral surfaces (M is Si, Al or other metals), and introduces special functional groups (e.g., −NH$_2$, −SH) to react with the polymer matrix. Accordingly, a network will be formed among clay mineral, silane and polymer via covalent bonds. This can greatly improve the mechanical property of the resultant materials and may lead to a breakthrough in synthesis of novel CPN

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(Herrera et al., 2004; Katsarava and Yakov, 1992; Kiliaris and Papaspyrides, 2010; LeBaron et al., 1999; Rong et al., 2006; Zhou et al., 2007).

The main aim of this review is to summarize the silylation methods of clay mineral surfaces and the related affecting factors. Although grafting of clay minerals with organosilanes goes back to the 1940s, the last decade is the most productive period, and some breakthroughs have been achieved. Literature about grafting methods in this review is chronologically restricted to those published during this period.

2. Sites in clay minerals for silane grafting

Successful silylation of clay mineral surfaces strongly depends on the reactivity of clay mineral surfaces, including internal surfaces, external surfaces and "broken" edges (Bergaya et al., 2006). Phyllosilicate surfaces contain two basic types, i.e., siloxane surface and hydroxyl surface. The 2:1 clay minerals (e.g., smectite group minerals) only contain siloxane surfaces while the 1:1 clay minerals (e.g., kaolinite group minerals) contain both the two kinds of surfaces.

Generally, the least reactive surface found on clay minerals under ambient conditions is the neutral siloxane surface that occurs on 2:1 phyllosilicates where no isomorphous substitution has occurred (e.g., talc and pyrophyllite), and on the Si-tetrahedral side of 1:1 kaolin group minerals (Bergaya et al., 2006; Charnay et al., 2001; Giese and Vanoss, 1993; Michot et al., 1994; Yariv, 1992). The existence of crystal defects (e.g., isomorphous substitution, vacancy and broken bond) can obviously increase the reactivity of the siloxane surface (Carrado et al., 2001). The hydroxyl surfaces (e.g., Al-octahedral surface in kaolinite) are excellent sites for grafting since the surface hydroxyls can condensate with alkoxyl group and/or the hydroxyls in the hydrolyzed silane (Brandt et al., 2003; Tonlé et al., 2007, 2011; Tunney and Detellier, 1993, 1996). Due to the high ratio of terminal surface area to the basal surface area, hydroxyl groups located at broken edges play an important role in the silane grafting reaction. However, due to the variation of structure and property of phyllosilicates, prominent difference of the grafting mechanism and grafting sites exists among different clay minerals. For swelling clay minerals such as montmorillonite, silane is readily intercalated into the interlayer space. Hence, all external surfaces, internal surfaces and "broken" edges are readily to be silylated under mild conditions (e.g., room temperature, no need of pre-intercalation) (He et al., 2005; Shen et al., 2007, 2009). Due to lack of swelling ability for non-swelling clay minerals such as kaolinite, pre-intercalation with small polar molecules is an indispensable step in the silylation of internal surfaces. This demands rigorous conditions for successful grafting such as high reaction temperature, inert atmosphere, and so on (Brandt et al., 2003; Tonlé et al., 2007, 2011).

3. Silylation of swelling clay minerals

For expandable clay minerals, all internal-surface, external surface and broken edge provide possible sites for silane grafting. Park (2004) successfully grafted octylsilane onto Laponite surface. The successful grafting did not increase the basal spacing, excluding the possibility of internal surface silylation. Similar studies (Daniel et al., 2008; Herrera et al., 2004, 2005) suggested that the broken edges of clay minerals are the most reactive sites for silane grafting. An important evidence is the decrease of Q^2 intensity with an increase of Q^3 intensity in ^{29}Si MAS NMR spectra after grafting reaction (Q stands for tetrafunctional units and the superscript is the number of bridging O atoms surrounding the silicon atom) (Lippmaa et al., 1980). In this case, the Q^2 signal corresponded to the Si located at the broken edges and the successful grafting resulted in a change of the Si local environment from Q^2 to Q^3. These studies also demonstrated that the trifunctional silane was grafted on the clay mineral edges in the

form of oligomers pillaring the clay mineral layers, whereas monofunctional derivatives selectively attached to the individual sheets (Herrera et al., 2004). A further study showed that the grafted amount and the grafting yield of silane were monitored as functions of the reaction time and the initial silane concentration (Herrera et al., 2005). These results show that the broken edges are the most reactive sites for silane grafting rather than external and internal surfaces for the 2:1 type synthetic swelling clay minerals. It is noteworthy that almost all these grafting reactions were carried out in toluene (nonpolar solvent), and little information is available on the influence of different solvents on the grafting reaction of these synthetic minerals.

Different from synthetic clay minerals, natural swelling clay minerals were readily intercalated by silane and/or polysiloxane oligomers during silane grafting (He et al., 2005; Shen et al., 2007, 2009), which could be judged by the increase of the basal spacing after grafting. For example, the basal spacing increased from 1.2 nm (pristine montmorillonite) to 1.8 nm (grafted products) after grafting montmorillonite with 3-aminopropyltriethoxysilane (APTES) (He et al., 2005; Shen et al., 2007, 2009). Meanwhile, two prominent T^2 [$Si(OSi)_2(OR')R$] and T^3 [$Si(OSi)_3R$] ($R = CH_2CH_2CH_2NH_2$, $R' = H$ or CH_2CH_3) signals were recorded in ^{29}Si MAS NMR spectra of the silylated products, implying the formation of polysiloxane oligomers. Unfortunately, the Q^2 signal was not observed in natural montmorillonites, which was readily recorded in 2:1 type synthetic clay minerals and attributed to the Si atoms located at broken edges. This may result from the higher crystallinity of natural clay minerals with a lower ratio of edge surface area to basal surface area than that of the synthetic clay minerals. Due to the lack of Q^2 signal, it is difficult to determine the grafting reaction occurring at the broken edges in natural montmorillonite.

Herrera et al. (2005) suggested that reaction conditions (e.g., reaction time, the initial silane concentration) had an important effect on the structure and property of the grafted products. So far, limited studies were reported about this aspect (Piscitelli et al., 2010; Shen et al., 2007, 2009). Shen and co-workers conducted a series of grafting reactions to elucidate the effect of reaction medium, number of functional groups in silane and characteristics of clay minerals on the structure of the silylated products (Shen et al., 2007, 2009). When the grafting reactions were conducted in ethanol–water mixture and vapor of silane, respectively, silane was readily intercalated into the montmorillonite interlayer spaces as indicated by a prominent increase of the basal spacing. The silylated products via vapor deposition had a larger basal spacing than that prepared in ethanol–water mixture, due to the different hydrolysis extent of silane in the two different systems. When the grafting reaction was conducted in silane vapor, silane was firstly intercalated into the interlayer spaces, and then hydrolysis and condensation occurred. In the system of ethanol–water mixture, silanes were readily to hydrolyze and form polysiloxane oligomers, resulting in the difficulty for intercalation of bulky oligomers. This could well explain that more silane was grafted onto montmorillonite in the case of silane vapor than that in ethanol–water mixture (Shen et al., 2007).

The number of functional groups in silane also has an important influence on the structure of the silylated products. Shen et al. (2007) reported that trifunctional APTES grafted montmorillonite displayed a basal spacing at 1.95 nm with a bilayer arrangement whereas monofunctional TMCS grafted products displayed a basal spacing at 1.47 nm with a monolayer arrangement. For monofunctional silane (e.g., TMCS), the silanol has two possible reaction ways, i.e., condensation with the surface hydroxyl of clay minerals or with silanol of another hydrolyzed silane molecule. For trifunctional silane (e.g., APTES), more than ten possible condensation ways can occur between silane and clay mineral, and among hydrolyzed silane molecules, resulting in complex structure in the silylated products.

The grafted silane amount was greatly increased on acid activated montmorillonite (Shen et al., 2009), due to the increased reactive sites generated through acid treatment (Breen et al., 1995, 1997; He et al., 2002). Meanwhile, an increase of reaction temperature and initial silane concentration would also facilitate the interaction between silanes and clay minerals, and lead to an increased amount of grafted silanes with respect to the intercalated species (Piscitelli et al., 2010).

Previous studies demonstrated that the maximum basal spacing of organoclay positively depended on the alkyl chain length of the surfactant used (Lagaly, 1981; Zhu et al., 2003). However, this kind of positive relationship between organic chain length and the basal spacing was not found in the silane grafted clay minerals. Piscitelli et al. (2010) reported that the longer the organic chain of aminosilane molecule, the smaller the basal spacing of the silylated montmorillonites. The molecular dynamics simulation displayed that the interactions among silane molecules (e.g., intermolecular hydrogen bonding) and between clay mineral and special group in silane (e.g., $-NH_2$ group) are important factors to control the basal spacing (Piscitelli et al., 2010).

Solvent is another important factor to govern the structure of the silylated products. Shanmugharaj et al. (2006) reported that the average basal spacing of grafted products was big when the solvents had relatively low surface energy but higher than the surface energy of montmorillonite. This means that both the dispersive and polar components of surface energy have an important influence on the basal spacing. The loaded silane in the silylated products included physically adsorbed silane, external- and internal-surface grafted silane, and intercalated silane. The grafting reaction contained two steps, i.e., adsorption and intercalation, followed by condensation reaction. This procedure strongly depended on the surface energy of the solvent as a dispersing medium. This finding can well explain why no silane intercalation was observed when the grafting reactions were conducted in nonpolar solvent (e.g., toluene) (Daniel et al., 2008; Herrera et al., 2004, 2005), and silanes were readily intercalated into the interlayer spaces in polar solvents (e.g., ethanol and water/ethanol mixture) (He et al., 2005).

On the other hand, in situ silylation technology was widely used in the synthesis of inorganic–organic hybrid phyllosilicates, such as 2:1 trioctahedral minerals (e.g., talc, hectorite and saponite) (Carrado, 2000; da Fonseca et al., 2000b; Fujii et al., 2003; Jaber et al., 2003; Silva et al., 2002), 2:1 dioctahedral minerals (e.g., pyrophyllite, beidellite and montmorillonite) (Jaber et al., 2005; Miehe-Brendle et al., 2010), and 1:1 minerals (e.g., kaolinite) (da Fonseca and Airoldi, 2000). The structure of inorganic–organic hybrid phyllosilicate strongly depended on the used metallic cations and organosilanes as silicon source in a sol–gel process. When divalent cations were used, the obtained hybrid phyllosilicates were trioctahedral minerals, whereas dioctahedral minerals was gained when trivalent cations were used (Burch, 1984; Carrado et al., 2001; da Fonseca et al., 2000b; Fujii et al., 2003; Jaber et al., 2005; Miehe-Brendle et al., 2010). The organosilanes with three hydrolysable functional groups (e.g., ethoxy group and methoxy group) were employed to build Si–O tetrahedral sheet, in which each silicon atom at the center of a tetrahedron was linked to the organic chain by a Si–C covalent bond.

All these synthetic hybrid phyllosilicates have some common features: 1) a layered structure without long-range periodicity (Jaber et al., 2005; Miehe-Brendle et al., 2010), resulting from the replacement of Si–O bonds by Si–C bonds in the tetrahedral sheets; 2) a large basal spacing, depending on the length of the attached alkyl chain; and 3) an improved organophilicity due to the organic chain of the organosilane.

Recently, Xue and Pinnavaia (2010) reported a new type of hybrid saponite with CH_2 groups substituting for bridging oxygen in the tetrahedral sheet, in which bis(triethoxysilyl)methane (BTESM) was used as silicon source. All the reflections of saponite were broadened and weakened with the increase of BETSM content, corresponding to a decrease of crystallinity and grain size. This resulted from the replacement of O atom in the Kagome lattice of mineral by the bridging methylene groups ($-CH_2-CH_2-$) and the ensued mismatch in bridging group size (Fig. 1). Although some details are still unclear about the structure of the hybrid saponite (e.g. the missing of T^3 signal), the report presented a novel way to synthesize hybrid minerals and silylate clay mineral surfaces.

4. Silylation of kaolinite

Different from 2:1 swelling clay minerals, the hydroxyl surface of Al-octahedra in kaolinite is possible sites for grafting reaction. But, it is difficult to directly intercalate kaolinite with silane due to the hydrogen bonding between neighboring kaolinite layers (Bergaya et al., 2006). To achieve a successful interlayer grafting, pre-intercalation with small polar molecules, e.g., dimethyl sulfoxide (DMSO) is an indispensable step to prepare an intercalate precursor, which will be used as substrate
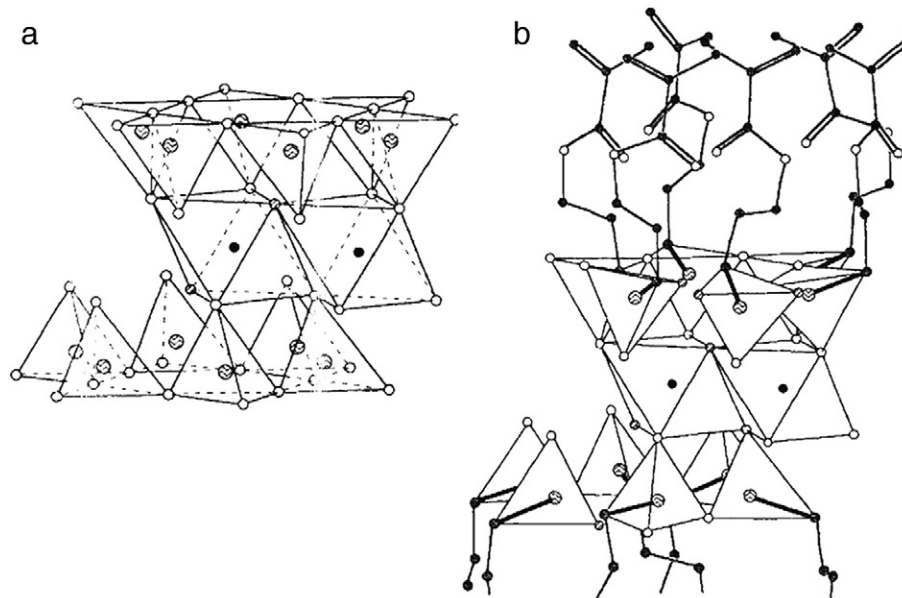

Fig. 1. Models for structures of (a) smectite and (b) new layered polymer: methacrylate–magnesium (nickel) phyllosilicate (⬡) Si, (●) Mg (or Ni), (○) O, (⊘) OH, (⬡) C (Xue and Pinnavaia, 2010).

for further organosilane intercalation and subsequent silylation. Tunney and co-workers conducted a series of pioneering work on the interlayer grafting of kaolinite (Brandt et al., 2003; Tonlé et al., 2007, 2011; Tunney and Detellier, 1993, 1996). A number of small-sized organics (e.g., ethylene glycol, methyl ether, 1,2-propanediol and 1,3-propanediol) were successfully applied in kaolinite grafting. Meanwhile, other researchers also reported successful grafting between the inner-surface hydroxyls of kaolinite and the small alcohol molecules, such as methanol, ethanolamine, D-sorbitol, adonitol, butanediols, and hexanol (Gardolinski and Lagaly, 2005; Itagaki and Kuroda, 2003; Murakami et al., 2004).

Recently, great efforts have been made to silylate kaolinite interlayer surfaces, and the introduced functional groups via silylation are capable of enduing the silylated products with versatile properties, such as organophilicity (Gârea et al., 2008), metal affinity (Tan et al., 2011) and enzyme loading (Hernando et al., 2007; Kim et al., 2006; Kobayashi and Matsunaga, 1991). A breakthrough about preparation of silane grafted kaolinite was achieved by Tonlé et al. (2007). The silane (APTES) was successfully grafted onto the interlayer surfaces of kaolinite at 195 °C when DMSO intercalated kaolinite was used as a precursor. The successful intercalation of APTES was evidenced by an increase of the basal spacing from 1.12 nm (DMSO intercalated kaolinite) to 1.64 nm (APTES grafted product).

Similar successful grafting was also reported by Avila et al. (2010), in which the grafting temperature was 200 °C. Three main reflections were recorded at 1.84, 1.00 and 1.13 nm. The reflections at 1.84 and 1.00 nm were attributed to two different arrangements of silane in the interlayer spaces while the one at 1.13 nm was due to the residual DMSO molecules in some interlayer spaces. More recently, Guerra et al. (2012) reported that silylated kaolinite was prepared by using APTES in the medium of dry toluene under an argon atmosphere, and the basal spacing was increased from 0.71 nm (pristine kaolinite) to 1.31 nm (silylated product). The prominent difference of the basal spacings in the silylated products indicates that the reaction conditions (e.g., reaction temperature, atmosphere and solvent) have a prominent influence on the interlayer structure of silylated products (Avila et al., 2010; Kobayashi and Matsunaga, 1991; Tonlé et al., 2007, 2011).

As indicated by literature (Avila et al., 2010; Tonlé et al., 2007, 2011), temperature was an important factor for successful silylation of kaolinite. To elucidate the influence of temperature on the grafting reaction, Yang et al. (2012) conducted a series of grafting reactions on kaolinite at different temperatures (175, 185, 195 and 220 °C). The temperatures of 175 and 185 °C are below the boiling point of DMSO (189 °C) while the temperature of 195 °C is higher than the boiling point of DMSO (189 °C) but lower than the boiling temperature of APTES (214 °C). The upper temperature was selected as 220 °C, at which the reactant mixture would be kept boiling but pyrolysis of APTES would not occur. The results showed that, at 175 °C, it was difficult for APTES to intercalate into the interlayer spaces of kaolinite. When temperature increased to 185 and 195 °C, APTES was intercalated into the kaolinite interlayer spaces with removal of the intercalated DMSO and subsequent condensation between APTES and kaolinite interlayer surface. In this case, the grafted APTES and the residual DMSO formed a pseudo-bilayer arrangement in the interlayer space, similar to those reported in literature (Avila et al., 2010; Tonlé et al., 2007). At 220 °C, the high temperature accelerated the diffusion of APTES into the kaolinite interlayer space as well as the removal of DMSO from the interlayer space. This also promoted the condensation between silanols of APTES and aluminols on kaolinite surfaces. As a result, a lateral-monolayer arrangement of the grafted APTES was formed in the interlayer space as shown in Fig. 2 (Yang et al., 2012). The amount of the grafted silane increased with the increase of reaction temperature. Table 1 gives a summary about recent reports of silane grafted kaolinites.

5. Concluding comments

The linkage between organic components and clay minerals via covalent bonds in silylated products can overcome most shortcomings of surfactant modified clays. Various methods and technologies have been applied in silylation of clay mineral surfaces. For non-swelling clay minerals such as kaolinite, pre-intercalation with polar small molecules is required for the further silylation of clay mineral surfaces. As demonstrated in the literature, temperature is a key factor to control
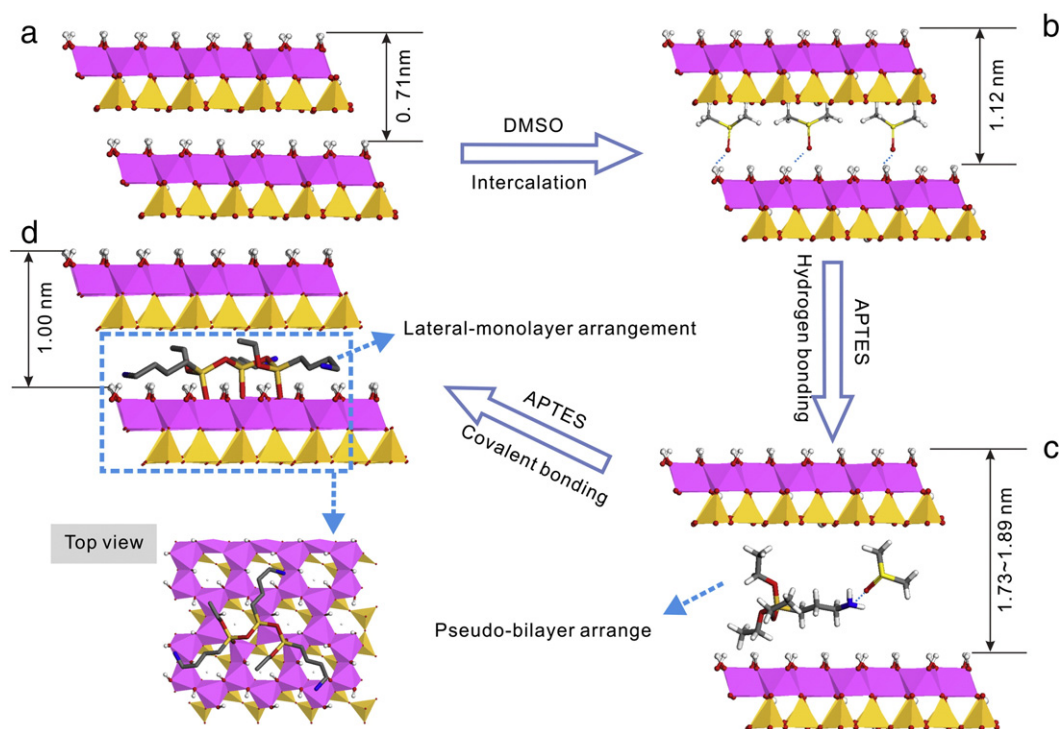

Fig. 2. Schematics of the grafting reaction between kaolinite and APTES (Yang et al., 2012).

Table 1
Summary of silane grafted kaolinites.

Authors	Intercalation reagent	Silane[a]	Medium[a]	Temperature and atmosphere	Reaction time (h)	d_{001} value (nm)
Tonlé et al. (2007)	DMSO/urea	APTES	APTES	195 °C, N_2	48	1.64
Avila et al. (2010)	DMSO	APTES	APTES	200 °C, N_2	48	1.84, 1.00
		MPTMS	MPTES			0.87
Tonlé et al. (2011)	DMSO	CPTES	CPTES	180–190 °C, N_2	24	0.90
Guerra et al. (2012)	DMSO	APTES	APTES, toluene	Reflux, Ar	8	1.31
de Faria et al. (2010)	DMSO	TRIS	TRIS	170 °C, N_2	48	1.27
Yang et al. (2012)	DMSO	APTES	APTES	175 °C, N_2	48	1.73, 1.00
				185 °C, N_2		1.81, 1.00
				195 °C, N_2		1.89, 1.00
				220 °C, N_2		1.00

[a] APTES: 3-aminopropyltriethoxysilane; MPTMS: 3-mercaptopropyltrimethoxysilane; TMCS: trimethylchlorosilane; CPTES: 3-chloropropyltriethoxysilane; and TRIS: tris(hydroxymethyl)aminomethanes.

the grafting reaction, i.e., the temperature higher than the boiling temperatures of both the intercalation reagent and the silane will facilitate grafting reaction. However, almost all reported studies showed that the silylated kaolinites maintained well-ordered structure and no exfoliation was observed. This is disadvantageous for preparation of CPN. Future studies could pay more attentions to exfoliation of silylated kaolinites during or after grafting reaction with help of other intercalation reagents, and the morphologies of the obtained products. For swelling clay minerals such as montmorillonite, the conditions for grafting reaction are not as rigorous as kaolinite does. However, there are still many debatable points about grafting mechanisms (e.g., the accurate grafting sites, condensation style). Molecular simulation and quantum calculation on the basis of the experimental conditions could be powerful technology to elucidate these problems in an atom scale.

In situ silylation during the synthesis of clay minerals is a feasible and promising way for obtaining silylated clay minerals. How to control the morphology of silylated products will attract scientific and technological interests. Synthesis and application of silylated clay minerals will be a highlighted field of clay science and may lead to a breakthrough in the field of CPN.

Acknowledgments

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