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Article

Interlayer structural and confined water effects in kaolinite–alcohol systems *via* dimethyl sulfoxide intercalation

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Abstract

Methanol- and ethylene glycol-grafted kaolinite were prepared *via* a stepwise intercalation–grafting strategy using dimethyl sulfoxide-intercalated kaolinite as an intermediate, with the aim of elucidating the structural differences between the two grafted products and clarifying the role of interlayer water. The products were systematically characterized by X-ray diffraction (XRD), Fourier-transform infrared (FTIR) spectroscopy, solid-state magic-angle spinning nuclear magnetic resonance (MAS NMR), elemental analysis (CHNS) and thermogravimetry–differential scanning calorimetry (TG–DSC). Compared with methoxy-modified kaolinite, the ethylene glycol-grafted kaolinite exhibited enhanced structural ordering, greater organic loading and improved thermal stability. The covalently grafted ethylene glycol molecules adopt a *trans* configuration in the interlayers of kaolinite, accompanied by a minute fraction of non-bonded ethylene glycol molecules and some amount of interlayer water molecules. Although the confined water in both systems originated from condensation reaction, it probably played opposite roles: it facilitated the ethylene glycol grafting while hindering that for methanol.

Keywords: Ethylene glycol; grafting; intercalation; kaolinite; methanol

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Kaolinite, with a structural formula $Al_2Si_2O_5(OH)_4$, is a naturally abundant 1:1 aluminosilicate composed of a tetrahedral silica sheet and an octahedral alumina sheet, held together by hydrogen bonds, dipole–dipole interactions and van der Waals forces (De Paiva *et al.*, 2008; Yuan *et al.*, 2013; He *et al.*, 2014). Due to its strong interlayer cohesion and low cation-exchange capacity, pristine kaolinite is only weakly reactive towards most organic molecules, resulting in a low degree of surface functionalization and limited application potential in advanced materials fields (Tunney & Detellier, 1993; Komori *et al.*, 2000; Yuan *et al.*, 2013). Consequently, developing effective strategies to modify the kaolinite interlayer space remains an important topic for further research.

Organic intercalation has long been recognized as an effective method to activate kaolinite by expanding its interlayer space and weakening the intrinsic hydrogen bonding (Bergaya & Lagaly, 2013; Dedzo & Detellier, 2016, 2018). The aluminol groups confined in the interlayer space of kaolinite could react with organic compounds, and a limited number of highly polar molecules or hydrogen bond donors, such as hydrazine, urea, formamide and dimethyl sulfoxide (DMSO; Johnston *et al.*, 1984; Frost *et al.*, 1998, 2000; Dedzo *et al.*, 2012; Cheng *et al.*, 2015b; Zhang *et al.*, 2015; Qiao *et al.*, 2020), can be directly intercalated. Additionally, the alkali salts of short-chain fatty acids (acetates, propionates, butyrates and isovalerates) can also be directly intercalated, such as potassium acetate (Bergaya & Lagaly, 2013). Among them, intercalation using polar molecules such as DMSO is a crucial pretreatment step that expands the interlayer space and increases the accessibility of internal hydroxyl groups. However, the disadvantage of intercalation is that most intercalated guest compounds are susceptible to desorption by washing with water or by heating (Dedzo & Detellier, 2016; Detellier, 2018).

By contrast, products obtained from grafting, whereby organic molecules form covalent bonds with kaolinite hydroxyl groups, demonstrated more functional groups, greater stability under certain conditions and a wider range of applications (Lagaly, 1981; Komori *et al.*, 1999, 2000; Janek *et al.*, 2007; De Faria *et al.*, 2010; Kuroda *et al.*, 2011; Dedzo *et al.*, 2012; Qiao *et al.*, 2014). The first interlamellar grafting of organic compounds in the kaolinite interlayer was reported by Tunney & Detellier (1993, 1994), in which DMSO- or *N*-methyl formamide-intercalated kaolinite was used as an intermediate and ethylene glycol and a series of diols were grafted. The resulting grafted structures typically involve Al–O–C, Al–O–Si and Al–O–CO linkages, leading to increased thermal stability and functional versatility (Letaief & Detellier, 2007; Avila *et al.*, 2010; De Faria *et al.*, 2010; Dedzo *et al.*, 2012; Hou *et al.*, 2014; Qiao *et al.*, 2017; Dedzo & Detellier, 2018).

Alcohols, such as methanol and ethylene glycol, have been widely used as grafting agents. Methoxy grafting, first achieved by Tunney & Detellier (1996) under extreme conditions and later reported at room temperature by Komori *et al.* (2000), produces a grafted layer with a stoichiometry of $Al_2Si_2O_5(OH)_{3.64}{\cdot}(OCH_3)_{0.36}{\cdot}0.58H_2O$ for the dried product. Subsequently, methoxy-modified kaolinite serves as an important

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intermediate for various guest species, such as alkylamines and quaternary ammonium salts (Gardolinski & Lagaly, 2005; Yuan *et al.*, 2013). The ethylene glycol-grafted kaolinite was first reported by Tunney & Detellier (1993), who described the covalently bonded 9.4 Å phase. Subsequently, two distinct derivatives with basal spacings of 10.8 and 9.4 Å were systematically prepared and characterized, and the critical role of water in controlling phase selectivity was elucidated (Tunney & Detellier, 1994). The 9.4 Å grafted phase, formed under anhydrous conditions, resists hydrolysis and withstands temperatures up to 350–400°C. Hirsemann *et al.* (2011) subsequently provided nuclear magnetic resonance (NMR) evidence for covalent Al–O–C bond formation, quantifying a grafting density of 0.6 ethylene glycol molecules per formula unit, corresponding to a composition of $Al_2Si_2O_5(OH)_{3.4}{\cdot}(OC_2H_4OH)_{0.6}$. Furthermore, the distance of ^{13}C–^{27}Al between the bonded carbon atom and the octahedral aluminium was determined to be 3.1 Å (Hirsemann *et al.*, 2011). The differences between the methanol- and ethylene glycol-grafted kaolinite thus lie not in the presence of covalent Al–O–C bonds but in the structural characteristics and stability of the resulting products. However, a direct comparative understanding of the two grafted systems remains lacking, which motivated the present study.

From a molecular perspective, the molecular size, hydroxyl functionality and hydrogen-bonding capability of methanol and ethylene glycol may lead to distinct interlayer coordination modes when grafted onto kaolinite. In particular, the role of the interlayer water generated during grafting reactions has been overlooked, despite its potential influence on molecular coordination and structural stability. A systematic understanding of how the molecular structure and interlayer water jointly control the formation, ordering and stability of alcohol-grafted kaolinite is still lacking.

In this study, methanol- and ethylene glycol-grafted kaolinite were synthesized using DMSO-intercalated kaolinite as a precursor. A comprehensive suite of characterization techniques, including X-ray diffraction (XRD), Fourier-transform infrared (FTIR) spectroscopy, solid-state magic-angle spinning nuclear magnetic resonance (MAS NMR), elemental analysis (CHNS) and thermogravimetry–differential scanning calorimetry (TG–DSC), was employed to elucidate the structural transformation, interlayer environment and thermal behaviour of the two grafting products. This work aims to clarify the role of alcohol functionality in controlling interlayer structure and stability and to provide new insights into the mechanism of alcohol grafting on kaolinite.

Materials

Well-crystallized kaolinite, with a Hinckley index of 1.31, was obtained from Hebei Province, China. The chemical composition, expressed as percentage by mass, is presented in Table 1. Analytical-grade ethanol, DMSO, methanol and ethylene glycol were purchased from Sigma Aldrich and used as received.

Table 1. The chemical composition by percentage mass of the original kaolinite.

SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO
46.01	0.91	35.63	0.55	0.08	0.01
MgO	CaO	Na_2O	K_2O	P_2O_5	LOI
0.45	0.32	0.18	0.15	0.15	15.3

LOI = loss on ignition.

Experimental

Sample preparation

The pre-intercalates, DMSO-intercalated kaolinite (Kaol-DMSO), were prepared by dispersing 2 g of kaolinite in a mixture of 18 mL DMSO and 2 mL deionized water at 90°C for 2 h. The obtained Kaol-DMSO compounds were centrifuged, washed with methanol and dried.

The synthesis of methanol- and ethylene glycol-grafted kaolinite was accomplished using the guest displacement method following literature procedures (Komori *et al.*, 2000; Gardolinski & Lagaly, 2005): 1 g of Kaol-DMSO was refluxed in 10 mL of methanol or ethylene glycol at boiling temperature for 24 h. The obtained powder was filtered, washed three times with ethanol and dried at 60°C for 12 h. The products were denoted as Kaol-MeOH and Kaol-EG, respectively.

Characterization

XRD analysis was performed using a Rigaku D/MAX 2500 PC diffractometer with Cu-*K*α radiation operating at 45 kV and 100 mA. The samples were scanned at 2°2θ min^{-1} in the range of 3°–60°. FTIR spectra of KBr pellets of samples were recorded on a Thermo Fisher Nicolet 6700 spectrometer (4000–600 cm^{-1}, 32 scans at 4 cm^{-1} resolution). Solid-state C and H NMR spectra were obtained under MAS conditions using an Agilent 600 DD2 NMR spectrometer.

Elemental CHNS analysis of grafted kaolinite was performed using an Elementar UNICUBE CHNS analyser (Germany) operating under dynamic combustion conditions. Each sample was analysed twice, and the average value was reported. The precision of duplicate measurements, expressed as relative standard deviation (RSD), was typically better than 1%.

TG–DSC was carried out using a simultaneous Netzsch STA 449 F3 thermal analyser. Measurements were taken at 30–1100°C with a heating rate of 10°C min^{-1} under a flowing nitrogen atmosphere (100 mL min^{-1}).

Results and discussion

Interlayer structural transformation revealed by XRD

The structural transitions occurring during the transformation from pristine kaolinite to the grafted products were recorded with XRD (Fig. 1). Raw kaolinite showed a diffraction maximum at 0.72 nm, corresponding to the typical (001) basal spacing of kaolinite layers. Upon DMSO intercalation, the (001) reflection shifted to a smaller angle with a basal spacing of 1.12 nm, confirming the intercalation of DMSO molecules into interlayer space of kaolinite (Johnston *et al.*, 1984; Zhang *et al.*, 2015).

When DMSO was replaced by alcohols, two distinct structural responses were observed. Subsequent grafting led to the disappearance of the DMSO-related (001) reflection and partial contraction of the interlayer space to 0.86 nm for methoxy-modified kaolinite and to 0.94 nm for ethylene glycol-grafted kaolinite. According to the calculation method proposed by Lagaly (2006; see also Tunney & Detellier, 1993, 1994), the intercalation ratios of methanol- and ethylene glycol-grafted kaolinite were determined to be 68.7% and 87.0%, respectively. In addition, the Hinkley index values of the two grafted products were evaluated, yielding values of 0.82 for methoxy-modified kaolinite and 1.23 for ethylene glycol-grafted

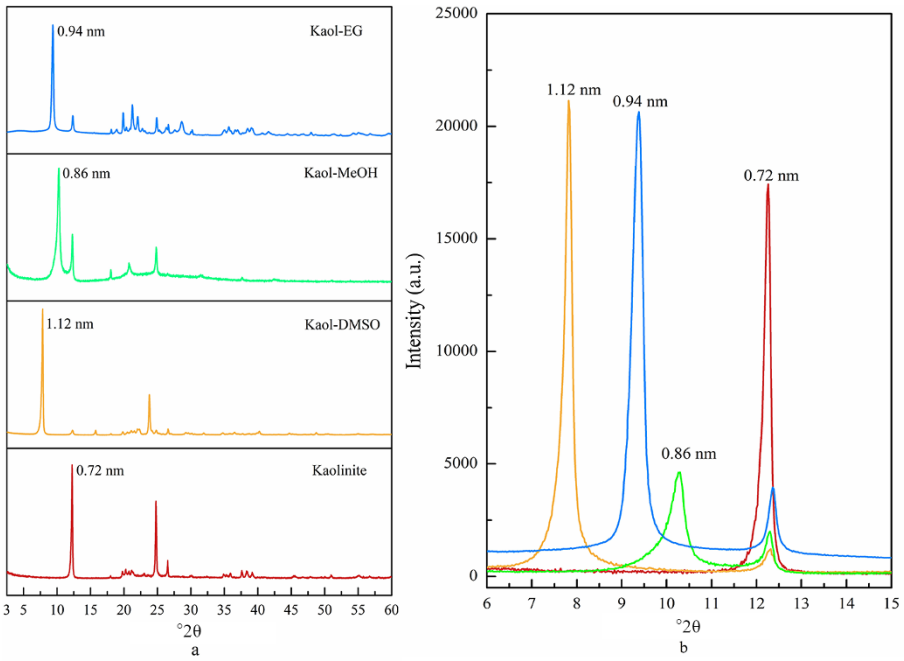


Figure 1. XRD traces of kaolinite, Kaol-DMSO, Kaol-MeOH and Kaol-EG: (a) full-range XRD traces and (b) enlarged (001) region.

kaolinite. This indicated that structural differences were formed by the two alcohol molecules within the interlayers of kaolinite.

Compared with methoxy-modified kaolinite, the ethylene glycol-grafted kaolinite displayed a more ordered interlayer structure. Methoxy-modified kaolinite displayed broader reflections with reduced intensity (Fig. 1b). By contrast, the ethylene glycol-grafted sample exhibited a sharper and more symmetric (001) reflection, indicating increased structural coherence and a more uniform interlayer environment. The full width at half maximum (FWHM) values, calculated in terms of 2θ, were 0.41 for methoxy-modified kaolinite and 0.29 for ethylene glycol-grafted kaolinite. These results indicated that, although both alcohols successfully replaced DMSO, the bifunctional characteristic of ethylene glycol promoted a more ordered interlayer structure.

Hydrogen bonding and chemical grafting evidenced by FTIR spectroscopy and MAS NMR

FTIR spectra confirmed the intercalation of DMSO into the interlayers of kaolinite (Fig. 2a). The FTIR spectra of pristine kaolinite displayed well-defined inner-surface O–H stretching bands and an inner-layer OH band (Fig. 2a). These features reflected the highly ordered hydrogen bonding framework inherent to the 1:1 layered structure. Upon DMSO intercalation, new bands emerged at 3538 and 3502 cm^{-1}, typical of S=O···H–O hydrogen bonds between DMSO molecules and the inner-surface hydroxyls of kaolinite (Johnston *et al.*, 1984; Zhang *et al.*, 2015). Moreover, new bands appeared at 3021 and 2936 cm^{-1}, corresponding to the bands of antisymmetric C–H stretching and symmetric C–H stretching, supporting the interlayer incorporation of DMSO (Madejová & Komadel, 2001; Cheng *et al.*, 2015a). The broad and less intense band at 1637 cm^{-1} was ascribed to the water molecules adsorbed on the external surface of kaolinite (Komori *et al.*, 1999, 2000). These results confirmed that strong host–guest interactions were formed within the interlayer and that some amount of water physically adsorbed on the external surface of Kaol-DMSO.

Following alcohol grafting, significant transformations in the C–H and O–H stretching regions were observed (Fig. 2a). Both grafted samples demonstrated that the O–H stretching bands of kaolinite were perturbed by the guest species, but the band due to the O–H stretching frequency of the inner hydroxyls at 3620 cm^{-1} remained unchanged. For the methanol-modified product, a broader and less intense O–H stretching region relative to pristine kaolinite was observed. As indicated by the significantly weakened bands at 3538 and 3502 cm^{-1}, DMSO molecules in the interlayer space of kaolinite were substituted by methanol. The band at 1653 cm^{-1} was assigned to H–O–H bending, indicating that some amount of water was present in the methoxy-modified kaolinite. The band at 3550 cm^{-1} was attributed to the hydrated kaolinite, indicating that hydrogen bonds were present between the OH groups of kaolinite and the interlayer water molecules. Due to factors such as hydrogen bond competition, steric hindrance coupled with interlayer space constraints and solvation effects leading to hydrogen bond network reorganization, this part of the water may serve as a significant inhibitor of the direct hydrogen bonding between kaolinite and methanol.

By contrast to the methoxy-modified kaolinite product, distinct differences were observed in the C–H and O–H stretching regions of the ethylene glycol-modified sample. The band at 3575 cm^{-1} was assigned to the hydrogen bonded component of the interlamellar surface hydroxyls of kaolinite, together with a hydrogen bonded O–H stretching frequency at 3387 cm^{-1} for the ethylene glycol moiety. Three distinct C–H stretching bands at 2894, 2943 and 2969 cm^{-1} were observed, different from that observed for neat ethylene glycol (Tunney & Detellier, 1994). In the region of the CH_2 deformation, four very weak bands at 1236, 1323, 1383 and 1462 cm^{-1} could be identified (Fig. 2b), for which the presence of the band at 1323 cm^{-1} was attributed to the *trans* conformation of the ethyleneoxy groups. The presence of C–O and C–H absorptions verified successful grafting through Al–O–C linkages, replacing the hydrogen bonded DMSO intercalate. The ethylene glycol molecules adopt a *trans* configuration in the interlayers of kaolinite, with the grafted product hosting a minute fraction

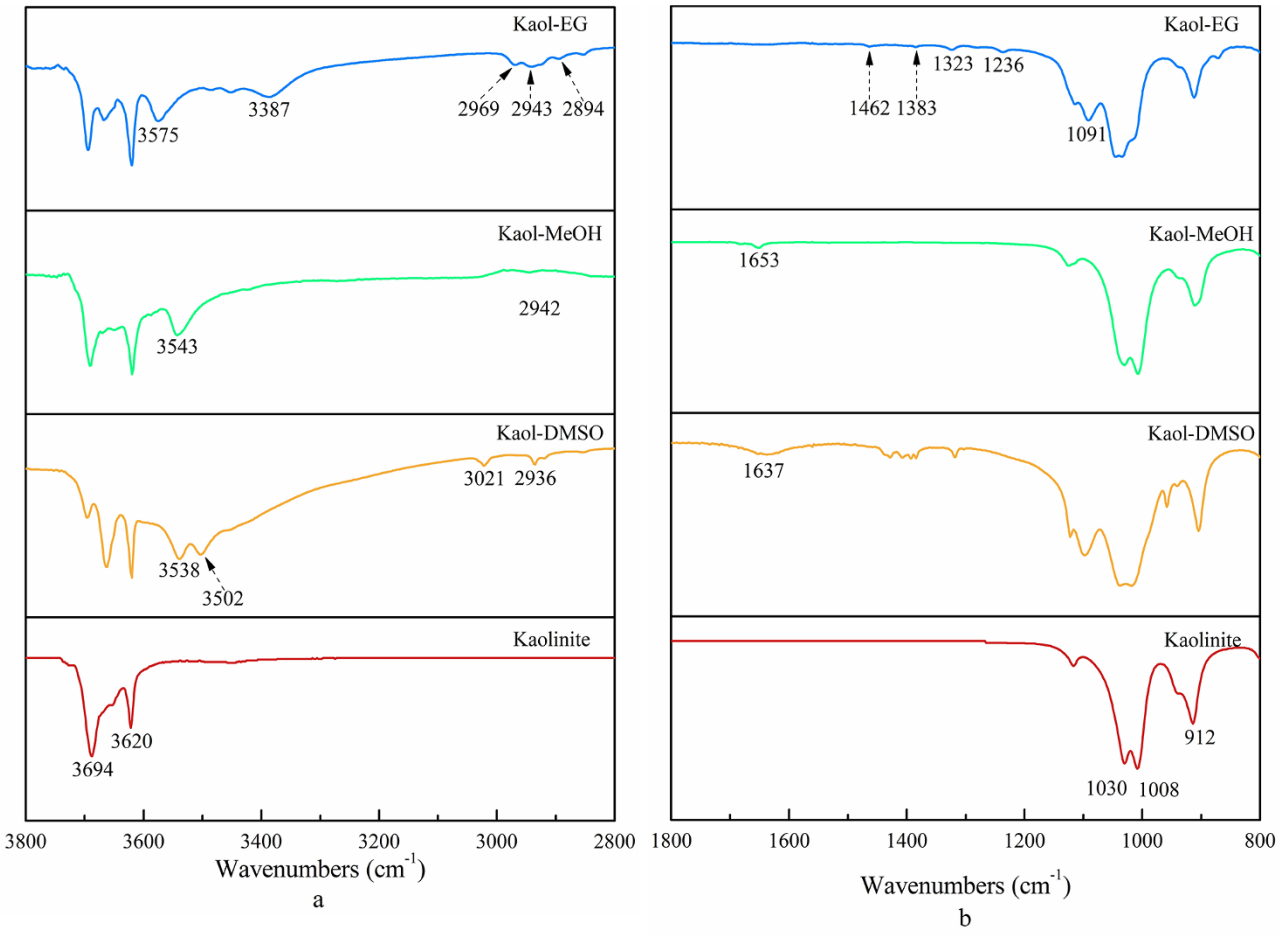


Figure 2. FTIR spectra of kaolinite, Kaol-DMSO, Kaol-MeOH and Kaol-EG in the regions of (a) 3800–2800 cm^{-1} and (b) 1800–800 cm^{-1}.

of non-bonded excess ethylene glycol and a measurable amount of water molecules. In contrast to the methanol-grafted product, although water may perturb the optimal Al–OH···ethylene glycol hydrogen bonds, ethylene glycol's structural advantages allow the system to accommodate and reorganize, potentially leading to a water-inclusive interlayer hydrogen bond network with retained stability.

The solid-state ^{13}C MAS NMR spectra revealed distinct bonding environments and interlayer structures among the Kaol-DMSO, methanol- and ethylene glycol-grafted samples (Fig. 3a). In general, the spectra transformed from a single DMSO-derived resonance to more shifted and defined alcohol-related signals, indicating transformation from hydrogen-bonded to covalently grafted configurations. Specifically, the Kaol-DMSO displayed a main resonance with slight splitting, consistent with previous work for confined DMSO, where two methyl groups experience non-equivalent local environments due to asymmetric hydrogen bonding (Thompson, 1985; Duer *et al.*, 1992). The methoxy-modified kaolinite showed a resonance at 51.5 ppm, representing the methyl carbon of the grafted methanol molecules. By contrast, the ethylene glycol-grafted sample exhibited a single sharp signal centred at 67.1 ppm, evidencing a uniform Al–O–C linkage (Tunney & Detellier, 1994) and a more compact, homogeneous interlayer arrangement of organic units.

The ^{1}H NMR spectra showed that water molecules are present in the Kaol-EG (0.94 nm; Fig. 3b). For ethylene glycol-grafted kaolinite, a weak but distinct resonance appears at 3.5 ppm, accompanied by broad shoulders near 2.0 and 4.8 ppm. The weak resonance at 3.5 ppm originated from $–CH_2–$ and –OH protons of grafted ethylene glycol, whereas the shoulders correspond, respectively, to residual surface hydroxyls and hydrogen-bonded water molecules confined in the interlayer. Compared with the spectra of DMSO and methanol derivatives, this profile highlights stronger hydrogen-bonding interactions and the retention of interlayer water in the ethylene glycol system, confirming the presence of a stabilized hydrogen bond network and a denser interlayer configuration (Hirsemann *et al.*, 2011).

Organic loading and water retention: insights from CHNS and TG–DSC analyses

The carbon, hydrogen and sulfur contents provide information regarding the chemical composition of the interlayer space of kaolinite, which was expected to change significantly upon intercalation of DMSO. Significant increases in carbon and sulfur contents were detected after DMSO intercalation (Table 2), consistent with the presence of the inserted DMSO molecules within the interlayer space. On the basis of sulfur content (7.53 mass%), the number of S=O groups (x) per $Al_2Si_2O_5(OH)_{(4-x)}$ was calculated to be 0.69 (for details, see the Supplementary Material), yielding a structural formula for the DMSO intercalated kaolinite $Al_2Si_2O_5(OH)_{3.31}\cdot(C_2H_6S)_{0.69}$. The calculated structural formula

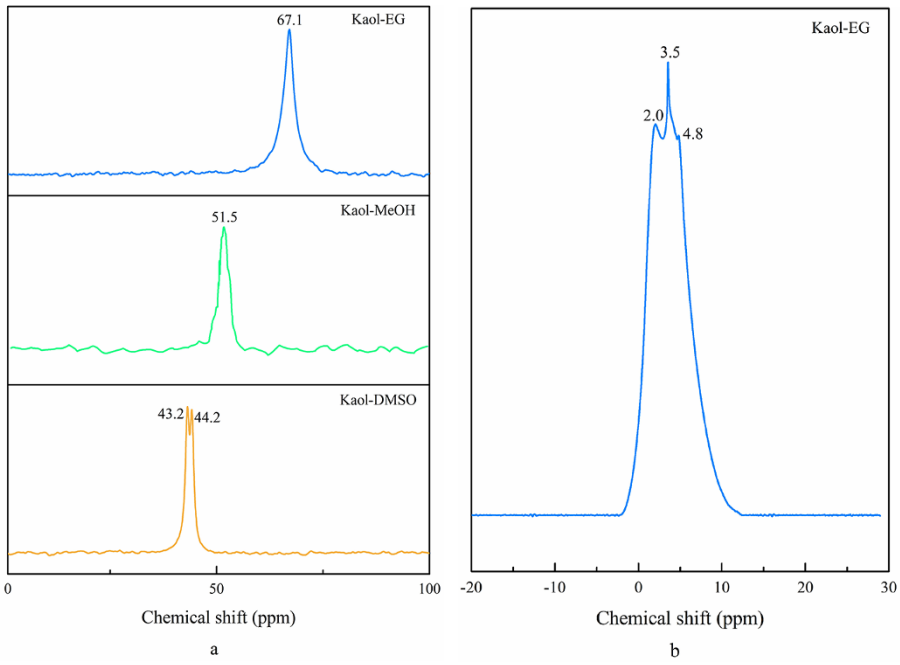


Figure 3. (a) ^{13}C MAS NMR spectra of Kaol-DMSO, Kaol-MeOH and Kaol-EG and (b) ^{1}H MAS NMR spectrum of Kaol-EG.

Table 2. Elemental contents (carbon, hydrogen, sulfur) of Kaol-DMSO, Kaol-MeOH and Kaol-EG and the calculated chemical formulas.

Sample		C (%)	H (%)	S (%)	Molar amount
Kaol-DMSO	Average[a]	5.75	2.47	7.53	$Al_2Si_2O_5(OH)_{3.31}\cdot(C_2H_6S)_{0.69}$
	AD	0.03	0.04	0.17	
	SD	0.02	0.03	0.12	
	RSD	0.003	0.01	0.02	
Kaol-MeOH	Average[a]	2.01	2.05	0.52	$Al_2Si_2O_5(OH)_{3.60}\cdot(CH_3O)_{0.36}\cdot(C_2H_6S)_{0.04}$
	AD	0.02	0.04	0.13	
	SD	0.01	0.03	0.08	
	RSD	0.01	0.01	0.02	
Kaol-EG	Average[a]	5.60	2.46	0.48	$Al_2Si_2O_5(OH)_{3.23}\cdot(OC_2H_4OH)_{0.73}\cdot(C_2H_6S)_{0.04}$
	AD	0.07	0.02	0.01	
	SD	0.05	0.01	0.01	
	RSD	0.01	0.01	0.01	

[a]All results were derived from duplicate experiments.
AD = absolute difference between the two measurements; SD = standard deviation.

was used to validate the contents of carbon and hydrogen, yielding values of 5.73% and 2.60%, respectively, which were in good agreement with the listed experimental data.

The structural formulae of methanol- and ethylene glycol-grafted kaolinite were also calculated based on the carbon and sulfur elemental contents, and the hydrogen elemental content was used for validation. As demonstrated earlier, residual sulfur in both grafted products indicated incomplete but substantial removal of DMSO. Consequently, the structural formulae derived from the carbon and sulfur contents were $Al_2Si_2O_5(OH)_{3.60}\cdot(CH_3O)_{0.36}\cdot(C_2H_6S)_{0.04}$ for methoxy-modified kaolinite and $Al_2Si_2O_5(OH)_{3.23}\cdot(OC_2H_4OH)_{0.73}\cdot(C_2H_6S)_{0.04}$ for ethylene glycol-grafted kaolinite.

As revealed by the structural formulae, the ethylene glycol grafting reaction consumed more hydroxyl groups, leading to organic loading of ethylene glycol molecules within the kaolinite interlayers that was approximately double that for methoxy-modified kaolinite. However, the calculated hydrogen content was smaller than the experiment data, indicating the presence of additional hydrogen sources, which originated from the condensation reaction between the Al–OH groups of kaolinite and the hydroxyl groups of the alcohols.

Figure 4 presents the TG and DSC curves of kaolinite, Kaol-DMSO, Kaol-MeOH and Kaol-EG under nitrogen. Pristine kaolinite exhibited a characteristic single-step mass loss (13.12%) associated with dehydroxylation that ranged from 400°C to 700°C, corresponding to the DSC peak centred at ~524°C. In contrast, two mass loss steps were observed in the TG curve of Kaol-DMSO: decomposition of DMSO molecules below 200°C and dehydroxylation of kaolinite near 480°C. The mass losses associated with these effects were calculated to 17.46% and 10.67%, respectively.

The grafted samples showed distinctly different thermodynamic responses. The methoxy-modified kaolinite exhibited a low-temperature (115–210°C) mass loss associated with water molecules, followed by a higher-temperature mass loss corresponding to dehydroxylation of the kaolinite from 360°C to 850°C. By contrast, three major mass loss steps were recorded in the TG curve of ethylene glycol-grafted kaolinite. The first mass loss step

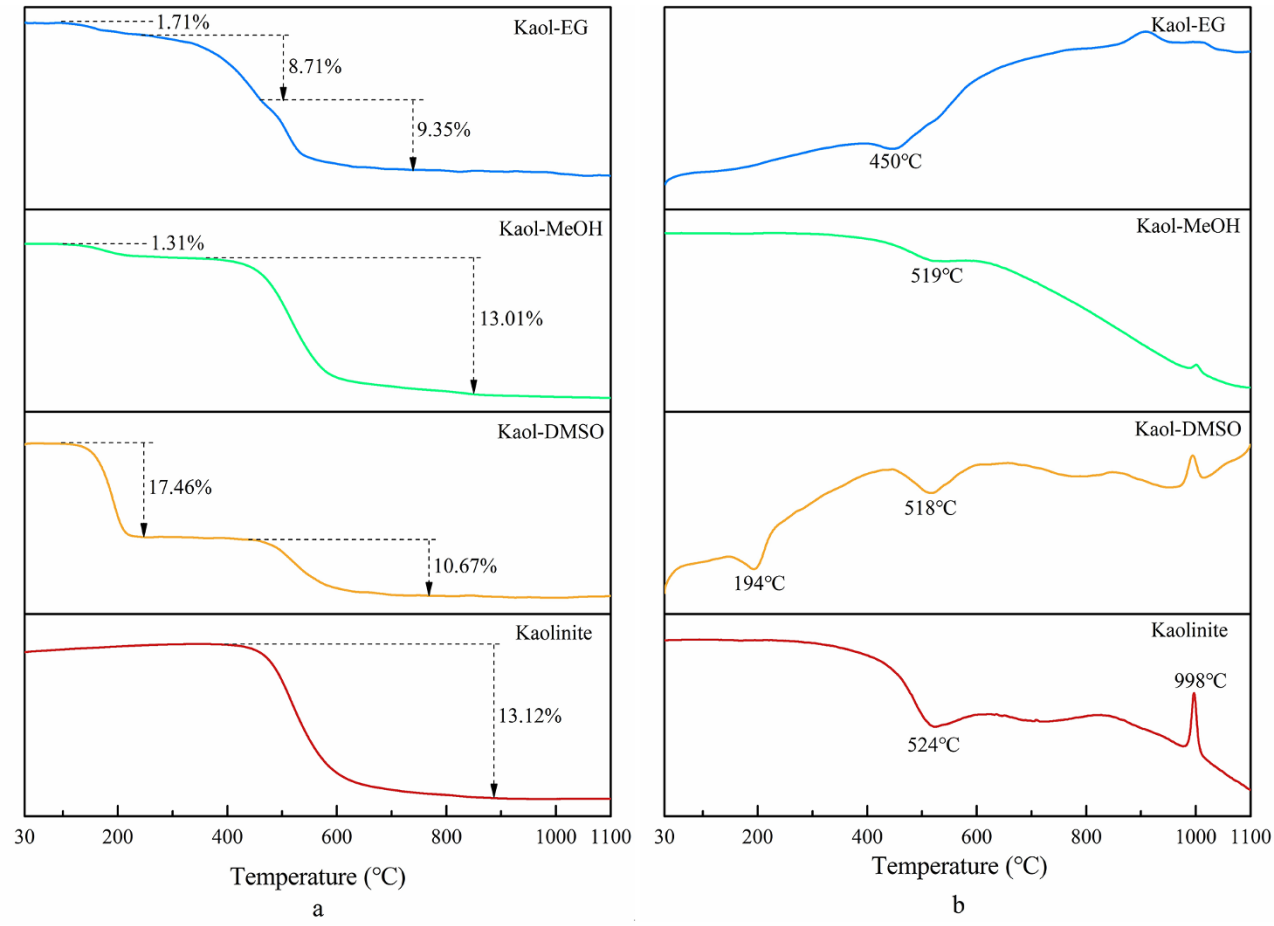


Figure 4. (a) TG and (b) DSC curves of kaolinite, Kaol-DMSO, Kaol-MeOH and Kaol-EG.

was clearly identified, but the second and third step partially overlapped. The first mass loss step at 100–200°C, corresponding to the DSC peak centred at ∼160°C, was ascribed to the removal of water molecules. The second mass loss at 250–460°C, corresponding to an 8.71% mass loss, was attributed to the removal of ethylene glycol molecules. The third 9.35% mass loss at 460–640°C was attributed to the dehydroxylation of kaolinite. Compared with the methoxy-modified kaolinite, a higher onset temperature for dehydroxylation was observed, reflecting the stronger interlayer binding and increased thermal stability of ethylene glycol-grafted kaolinite.

Formation mechanism of methanol- and ethylene glycol-grafted kaolinite

The transformation sequence is summarized schematically in Fig. 5. In this stepwise intercalation–grafting reaction, DMSO molecules, possessing a high dipole moment (4.0 Debye) and strong S=O···H–O bonding capability, intercalated directly into the interlayer space of kaolinite and acted as an essential 'interlayer template', expanding the basal spacing and weakening the Al–OH···O–Si network. DMSO is a strong hydrogen bond acceptor, enabling it to form strong hydrogen bonds with the inner-surface Al–OH groups and create Al–O–S bonds. Subsequent treatment with methanol or ethylene glycol led to the substitution of relatively weak Al–O–S interactions by stronger covalent Al–O–C bonds. The overall displacement reaction was thermodynamically spontaneous due to this exchange being towards a higher bond strength and a more stable grafted structure.

The water molecules generated by a condensation reaction may have a significant impact on the arrangement of alcohols and the stability of grafting products. For methanol-grafted products, water molecules may have competed with methanol for the Al–OH groups of kaolinite, forming hydrogen bonds that block grafting. In addition, the presence of water also introduced steric constraints that prevented methanol from achieving a favourable orientation. Consequently, some methanol molecules may have interacted indirectly with Al–OH *via* water bridges (Al–OH···OH_2···$HOCH_3$), forming a weaker, reorganized hydrogen bond network and so producing a disordered and poorly crystalline methoxy-modified kaolinite.

By contrast with methanol, ethylene glycol functions as a bidentate ligand, offering more binding sites and granting ethylene glycol greater competitiveness, enabling it to partially displace or coexist with water molecules at the interface. Spatially, the ethylene glycol-grafted kaolinite provided more space to accommodate water, thereby reducing steric hindrance and facilitating water molecules to integrate into the complex hydrogen bond network. Therefore, water was not only a disruptor but also could be incorporated into a hybrid network. As a result, the interlayer structure, organic loading and thermal stability collectively demonstrated that the

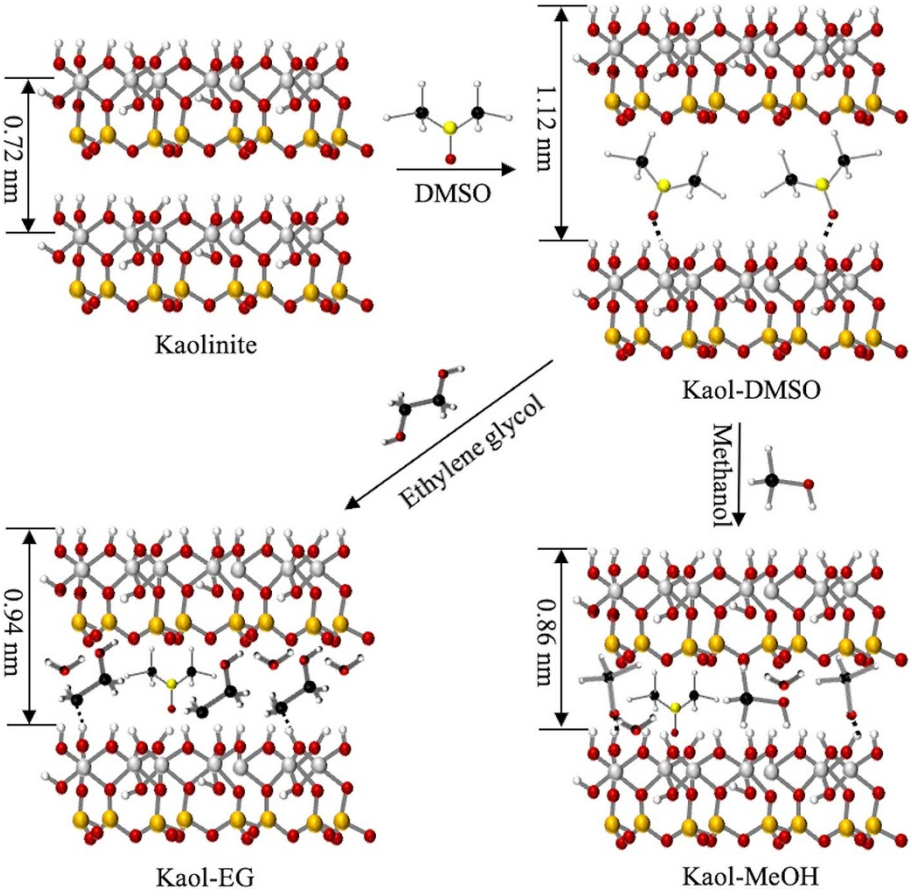


Figure 5. Schematic representation of the transformation from kaolinite to Kaol-DMSO, Kaol-MeOH and Kaol-EG. Al = dark grey; C = black; H = white; O = red; Si = yellow.

ethylene glycol-grafted kaolinite exhibited a more stable, chemically integrated grafted configuration than its methanol counterpart, reflecting a balance between steric accessibility and hydrogen bond-mediated cohesion. Thus, the interlayer structure and bonding mechanism of grafting were presumably influenced by the molecular polarity, size, hydrogen-bonding capacity and steric hindrance of the substituent alcohols, as well as by the presence of confined water.

Conclusions

The ethylene glycol-grafted kaolinite exhibited a more ordered and compact grafting structure than its methoxy-modified counterpart, and water molecules coexisted with ethylene glycol in the interlayer space. This difference was controlled by a combination of molecular properties (polarity, size, hydrogen-bonding capability) and their synergy with confined water molecules. Notably, water molecules appeared to play an adverse role in methanol and ethylene glycol grafting.

Supplementary material. The supplementary material for this article can be found at https://doi.org/10.1180/clm.2026.10061.

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Competing interests. The authors declare that they have no financial or personal relationships with other people or organizations that can inappropriately influence their work described in this paper. There are no professional or other personal interests of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in the enclosed article.

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