

PREPARATION AND CHARACTERIZATION OF TWO DISTINCT ETHYLENE GLYCOL DERIVATIVES OF KAOLINITE

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Abstract—A new, well-ordered, thermally robust ethylene glycol intercalate of kaolinite was formed by refluxing the dimethyl sulfoxide intercalate of kaolinite (Kao-DMSO) with dry ethylene glycol (EG). This new phase (Kao-EG 9.4 Å) which is characterized by a d_{001} of 9.4 Å is distinct from a previously reported ethylene glycol intercalated phase of kaolinite (Kao-EG 10.8 Å) which has a d_{001} of 10.8 Å. The characterization of these two phases was studied by XRD, NMR, FTIR, and TGA/DSC. It was found that the concentration of water in the ethylene glycol reaction media played a crucial role in governing which of the phases predominated. Water favored Kao-EG 10.8 Å formation, while anhydrous conditions favored the formation of Kao-EG 9.4 Å. It is hypothesized that Kao-EG 9.4 Å is a grafted phase resulting from the product of the condensation reaction between an aluminol group on the interlamellar surface of kaolinite and the alcohol group of ethylene glycol. Ethylene glycol units would be attached to the interlamellar surface of kaolinite via Al-O-C bonds. The Kao-EG 9.4 Å phase was found to be resistant to both thermal decomposition up to 330°C and also, once formed, in the absence of interlamellar water molecules, to decomposition by hydrolysis in refluxing water.

Key Words—Ethylene glycol, Interlamellar modification, Kaolinite.

INTRODUCTION

Several organic intercalates of kaolinite have been reported over the years (Theng 1974; Raussell-Colom and Serratos 1987; MacEwan and Wilson 1984). Most of these intercalation complexes involve the penetration of small polar molecules into the interlamellar space of kaolinite, thus prying open the clay layers. A select number of molecules, which include dimethyl sulfoxide (DMSO), N-methyl formamide (NMF) and hydrazine, may be intercalated directly into kaolinite by simply exposing kaolinite to these substances in their vapor or liquid states for sufficient periods of time (Olejnik *et al* 1970). Other small molecules may also be intercalated, but only indirectly by displacing a previously intercalated molecule (MacEwan and Wilson 1984; Camazano and Garcia 1966; Olejnik *et al* 1970). It has also recently been shown that it is possible to trap polymers in the interlamellar spaces of kaolinite by first intercalating the appropriate monomer and then thermally inducing polymerization (Sugahara *et al* 1990; Sugahara *et al* 1988).

Another type of interlamellar modification involves surface grafting, or the actual formation of covalent bonds to the interlamellar surface of kaolinite. This type of modification is expected to produce more thermally and chemically robust materials. The grafting of borates to the interlamellar surface of kaolinite to yield a material which is thermally stable up to 400°C and which is not washed out with water has been reported (Ovramenko *et al* 1989). Recently, we reported an example of the grafting of organic units to the interlamellar surface of kaolinite (Tunney and Detellier 1993). This involved the attachment of various alcohols to

the aluminate surface of kaolinite. Especially studied, was a 9.4 Å ethylene glycol derivative of kaolinite. This material exhibited thermal stability much beyond that expected for an intercalate, and could not be washed out with water or other solvents. The interlamellar clearance space of 2.3 Å corresponded with what may be expected from a grafted ethylene glycol species. The existence of a 10.8 Å ethylene glycol intercalated kaolinite had been described in the late 1960's (Camazano and Garcia 1966; Range *et al* 1969), and recently an 11.0 Å ethylene glycol intercalate of an 8.4 Å hydrated kaolinite was reported (Costanzo and Giese 1990). However, a 9.4 Å phase has never been reported, despite the fact that one of the groups (Camazano and Garcia 1966) used virtually identical conditions in the synthesis of their intercalated phase as was used in the synthesis of the 9.4 Å grafted phase (Tunney and Detellier 1993). The question arises: what governs the formation of the intercalated ethylene glycol 10.8 Å phase of kaolinite over that of the 9.4 Å phase? In this paper an attempt is made to answer this question as well as to better characterize these two phases in the hope of better understanding some of the chemistry which can occur between alcohols and the interlamellar surfaces of kaolinite and possibly other similar materials.

BACKGROUND

Kaolinite is a 1:1 layered clay composed of repeating layers of a tetrahedral silicate sheet that shares oxygen with an octahedral aluminate sheet in an extended two-dimensional network. The surface silicate sheet is comprised of hexagonal $-(\text{SiO})_6$ macrorings and the surface

aluminate sheet is covered with aluminol groups (Al-OH) (Bailey 1984; Giese 1988).

The forces which keep the kaolinite layers together are believed to be the summation of van der Waals attractive forces, hydrogen bonding between adjacent layers and electrostatic interactions due to net fractional charges of opposite sign on each basal surface, with the main contribution coming from the electrostatic term (Cruz *et al* 1972). With this in mind, the driving force for intercalation involves the "solvation" of the dipolar kaolinite layers with the intercalating agent.

As previously stated, intercalation may not be the sole process responsible for the interlamellar modification of kaolinite. It is conceivable that in some cases, the covalent grafting of molecules onto the interlamellar surface of kaolinite may indeed be a competing process. While the surface silicate sheet of kaolinite is not particularly amenable to covalent bond attachment, the relatively reactive aluminol surface has the potential to be functionalized via Al-O-R bonds. It is known for example, that alcohols may condense with the aluminol groups on the surface of alumina to give surface ethers (Al-O-R) (Greenler 1962; Boreskov *et al* 1964) and there are several examples of functionalized aluminas being used in chromatography and catalysis (Tundo *et al* 1982). These materials are the products of the condensation reactions between reactant molecules and the surface aluminol groups. Recently, Inoue and co-workers described the synthesis and characterization of a number of diol and aminoalcohol modified boehmite materials (Inoue *et al* 1988, 1991a, 1991b). Since the aluminate surface of boehmite is similar to that of kaolinite, it is reasonable to assume that similar reactions should be possible for kaolinite assuming that access can be provided to the interlamellar spaces.

EXPERIMENTAL METHODS

Materials

Well-crystallized Georgia kaolinite (KGa-1) was obtained from the Source Clay Repository of the Clay Mineral Society and was purified by sedimentation. The <2 μm esd fraction (>98% of the sample, as determined by particle size analysis on a Sedigraph 5100) was used in all the experiments. Characterization of the purified kaolinite by XRD, FTIR and TGA all confirmed the purity of the material. Ethylene glycol was fractionally distilled to remove most of the water (<500 ppm by Karl Fischer titration). All other chemicals were reagent grade and used without further purification.

Synthesis

The dimethyl sulfoxide intercalate of kaolinite (kao-DMSO) was prepared by mixing typically 20 g of the

purified kaolinite in 100 mL of DMSO and allowing sufficient time (2 months) for maximum intercalation to occur as judged by measuring the XRD patterns of the sample smeared onto a glass slide and comparing the peak intensities of the intercalated versus the non intercalated d_{001} peaks. The sample was then filtered and washed with 50 mL dioxane to remove excess DMSO. After air drying for four hours, 31 g of white powder was collected and characterized by XRD, FTIR and TGA/DSC before proceeding further. It was estimated by powder XRD that 92% of the product was in the intercalated form ($d_{001} = 11.2 \text{ \AA}$), with the remaining product existing as the unexpanded kaolinite ($d_{001} = 7.2 \text{ \AA}$).

Kao-DMSO was then reacted with refluxing ethylene glycol : water mixtures to obtain various ethylene glycol functionalized organo-kaolinites. Typically, 1 g of the Kao-DMSO was dispersed in 50 ml of an ethylene glycol : water mixture for 16 h under nitrogen atmosphere. Workup consisted of filtering the product and washing with 30 ml of dioxane followed by air drying. No DMSO could be detected after the work-up, as evidenced by the absence of its characteristic bands in IR and of its CPMAS ^{13}C NMR signal (see Figure 6).

Characterization methods

All FTIR spectra were performed on a Bomem Michelson MB 100 spectrometer using the KBr pellet technique. Thirty scans were acquired with a resolution of 4 cm^{-1} . Powder X-ray diffraction was done on a Philips PW3710 spectrometer with $\text{CuK}\alpha$ radiation. Samples were prepared for XRD measurements by dispersing about 20 mg of sample in ethanol and then applying the dispersion on a glass slide and allowing to air dry. TGA measurements were taken with a Polymer Labs STA 1500H with alumina reference and sample pans under flowing nitrogen (40 cc/min) and a heating rate ranging from 15 to 20°C per minute. The ^{13}C CP/MAS and DD/MAS (dephasing period of 40 μs) were recorded at 75.37 MHz on a Chemagnetics CMX-300 spectrometer, with a spinning rate of 7 kHz.

RESULTS

The role of water in governing product formation

The formation of a 10.8 \AA ethylene glycol intercalate of kaolinite (Kao-EG 10.8 \AA) has been previously reported (Camazano and Garcia 1966; Range *et al* 1969), however the existence of a 9.5 \AA ethylene glycol derivatized organo-kaolinite was only recently reported (Tunney and Detellier 1993). Better powder XRD analysis has now shown that it is more accurate to describe this phase as a 9.4 \AA organo-kaolinite (Kao-EG 9.4 \AA). In an attempt to understand some of the factors which govern the formation of one ethylene glycol organo-kaolinite over another, a series of experiments were performed whereby the initial water content of the re-

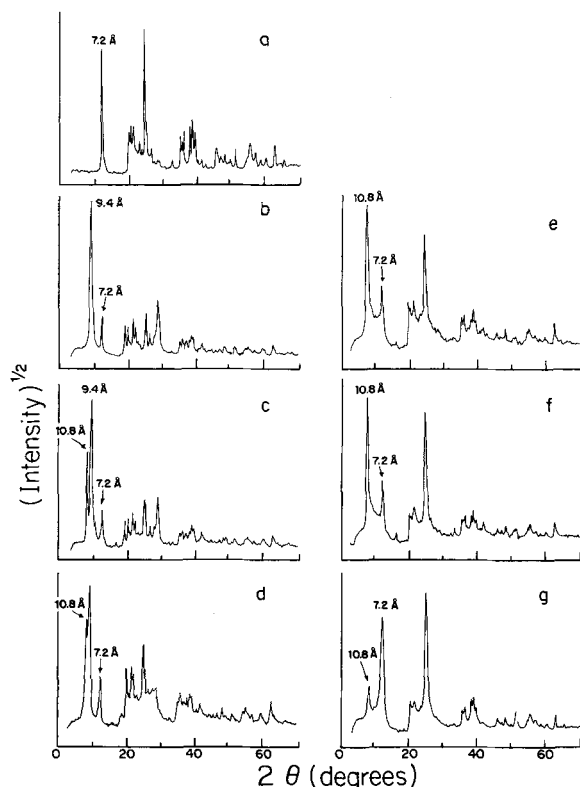


Figure 1. Powder XRD patterns of: kaolinite starting material (a) and Kao-EG samples prepared with 0% (b), 1% (c), 2% (d), 5% (e), 10% (f) and 20% (g) by volume water added to the refluxing ethylene glycol/Kaolinite:DMSO reaction mixture (see experimental section for details).

action media was varied from close to 0% by volume to 20% by volume. The powder XRD patterns of the products of these trials are shown in Figure 1. It was found that by changing the water content of the reaction media it was possible to change the nature of the products. The results taken from Figure 1 are summarized in Table 1. The product distribution was roughly estimated on the basis of the relative intensities of the basal peaks of the various product phases. It was found to be a function of the water content of the reaction media.

When Kao-DMSO was refluxed in relatively dry ethylene glycol (trial 1), the main product was the 9.4 Å ethylene glycol modified organo-kaolinite "Kao-EG 9.4 Å". Residual unexpanded kaolinite contaminates the product in this and all other trials, and is seen as the superposition of the powder XRD patterns of unexpanded kaolinite onto that of the principal product(s). This is not surprising since the Kao:DMSO starting material contains approximately 7% unexpanded kaolinite as judged by comparing the relative heights of the basal reflections of the DMSO intercalated ($d_{001} = 11.2$ Å) and unexpanded ($d_{001} = 7.2$ Å) kaolinite.

As the water content was increased, another ethylene

Table 1. Data showing the dependence of product formation on the water content of the reaction mixture. The trials involved refluxing Kao:DMSO with the given ethylene glycol/water mixtures (see the experimental section). The product distribution was analyzed by measuring the relative intensities of the d_{001} peaks of the various phases with the sum total basal spacing intensity normalized to 100.

Trial #	Percentage of water in reaction mixture ¹	Relative intensities of the d_{001} XRD peaks of products (as a percentage of the total intensity)		
		Kao:EG 10.8 Å phase	Kao:EG 9.4 Å phase	Residual Kaolinite 7.2 Å phase
1	0.0	—	93.7	6.3
2 ²	1.0	32.3	61.3	3.9
3	2.0	38.7	53.9	7.4
4	5.0	87.3	—	12.7
5	10.0	87.7	—	12.3
6	20.0	12.2	—	87.8

¹ The reaction mixtures were prepared by adding a given volume of water to dry ethylene glycol (<0.05% by Karl Fischer titration). The percentage of water was taken as the percent volume of water per sum total volume before mixing.

² The product distribution does not add up to 100% since an additional 2.5% was in the form of an 8.4 Å hydrate of kaolinite (Figure 1c) (Tunney and Detellier 1994).

glycol modified organo-kaolinite was observed with a characteristic basal spacing of 10.8 Å (Kao-EG 10.8 Å). In trials 2 and 3, at low concentrations of water (1% and 2% by volume respectively), the Kao-EG 9.4 Å phase was still predominant, but as the water content was increased still further to 5% and 10% (trials 4 and 5), Kao-EG 10.8 Å became the predominant product and the Kao-EG 9.4 Å phase could not even be detected. At still higher concentrations of water (trial 6), the yield of Kao-EG 10.8 Å was dramatically reduced and the formation of unexpanded kaolinite material became the principal phase. This shows that there is an optimum water content for the reaction media if one wishes to maximize the yield of Kao-EG 10.8 Å. In contrast, to maximize the yield of the Kao-EG 9.4 Å phase, it is required that the reaction media consist of dry ethylene glycol.

Characterization of Kao-EG 9.4 Å and Kao-EG 10.8 Å

Characterization of the Kao-EG 9.4 Å and the Kao-EG 10.8 Å phases was hampered by the fact that it was not possible to obtain solely one phase. Nonetheless, it was possible through use of an assortment of techniques to gain some insight into the structures of these two phases as well as the relationship between the two. It was decided to more fully characterize the products of trials 1, 4 and 5 (see Table 1 and Figures 1b, 1e, and 1f) since these runs had the highest yields of Kao-EG 9.4 Å (trial 1) and Kao-EG 10.8 Å (trials 4, 5).

Thermogravimetric analysis. The TGA curves for kaolinite, Kao-EG 9.4 Å and Kao-EG 10.8 Å are given

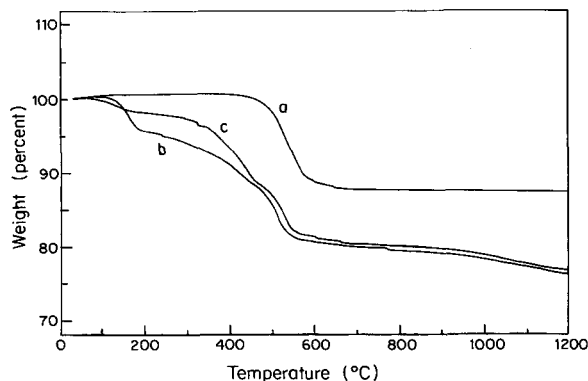


Figure 2. TGA results for: (a) kaolinite starting material; (b) Kao-EG 10.8 Å (trial 5) and (c) Kao-EG 9.4 Å (trial 1).

in Figure 2. Kaolinite exhibits a single weight loss of 13.1% from 400 to 700°C ($T_{\text{ons.}} = 478^\circ\text{C}$) corresponding to the loss of water in the dehydroxylation reaction of the crystal structure in the kaolinite-metakaolinite phase transition (Earnest 1980). The corresponding DSC run (not shown) showed an endothermic transition at 538°C (peak minimum) corresponding to the 13.1% weight loss as well as a sharp exothermic transition at 1003°C (peak maximum) corresponding to a structural reorganization (no weight change) of metakaolinite (Perez-Maqueda *et al* 1993).

Kao-EG 10.8 Å exhibits a weight loss of 5.4% at an onset temperature of 124°C and a slow two step weight loss of 14.5% beginning at around 240°C and ending at 620°C. The first decomposition in this two step process occurs in the range of 240–440°C ($T_{\text{ons.}} = 343^\circ\text{C}$) and involves a 5.1% weight loss. The second decomposition step occurs in the range 440–620°C ($T_{\text{ons.}} = 486^\circ\text{C}$) and involves a weight loss of 9.4%. From 620°C to 1200°C an additional 4.2% weight loss occurs. The DSC run (not shown) gives endothermic minima at 160°C, 426°C, and 524°C corresponding to the 5.4, 5.1 and 9.4% weight losses. In addition to the exothermic peak maximum at 1003°C (metakaolinite structural organization), there is a smaller exotherm maximum at 1025°C.

Kao-EG 9.4 Å experiences its first weight loss of 2.1% in what appears to be a two step process from 60–200°C. The DSC run shows a 2-stage endothermic event with peaks at 100°C and 145°C. The next weight loss involves another 2-stage decomposition between 200°C and 620°C. The first stage occurs from 200–470°C ($T_{\text{ons.}} = 346^\circ\text{C}$; 9.8% weight loss) and the second stage occurs from 470–620°C ($T_{\text{ons.}} = 507^\circ\text{C}$; 7.2% weight loss). The DSC run shows endothermic minimum at 444°C, and 554°C as well as an exotherm at 528°C. Finally, from 620°C to 1200°C there is a gradual 4.3% weight loss. DSC show two exotherms at 1004°C and 1029°C similar to what was obtained for Kao-EG 10.8 Å except that in this case, the 1029°C exotherm is larger than the 1004°C exotherm.

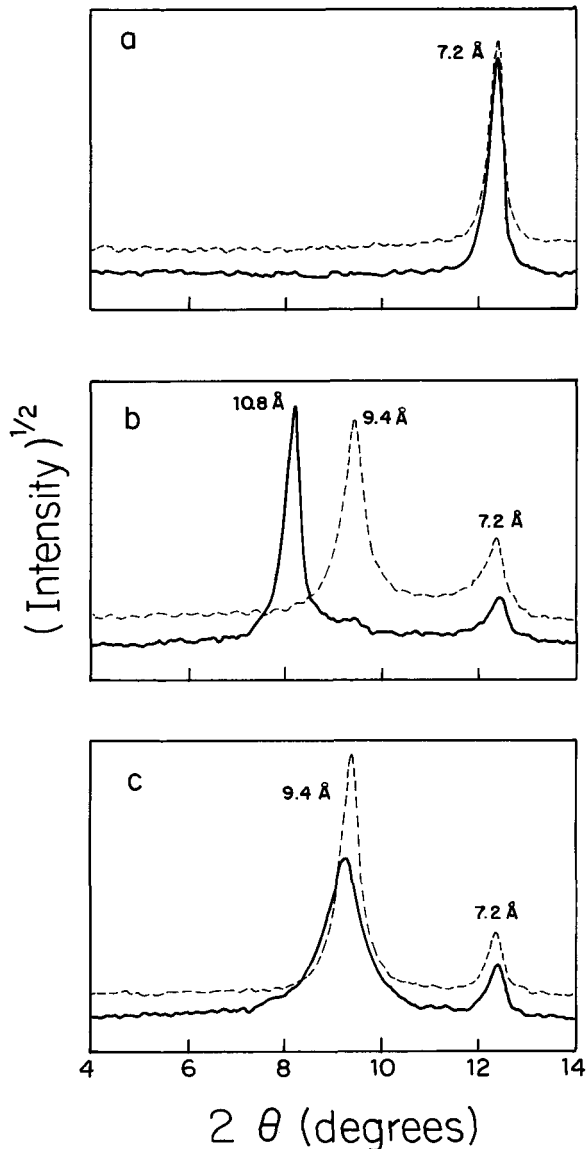
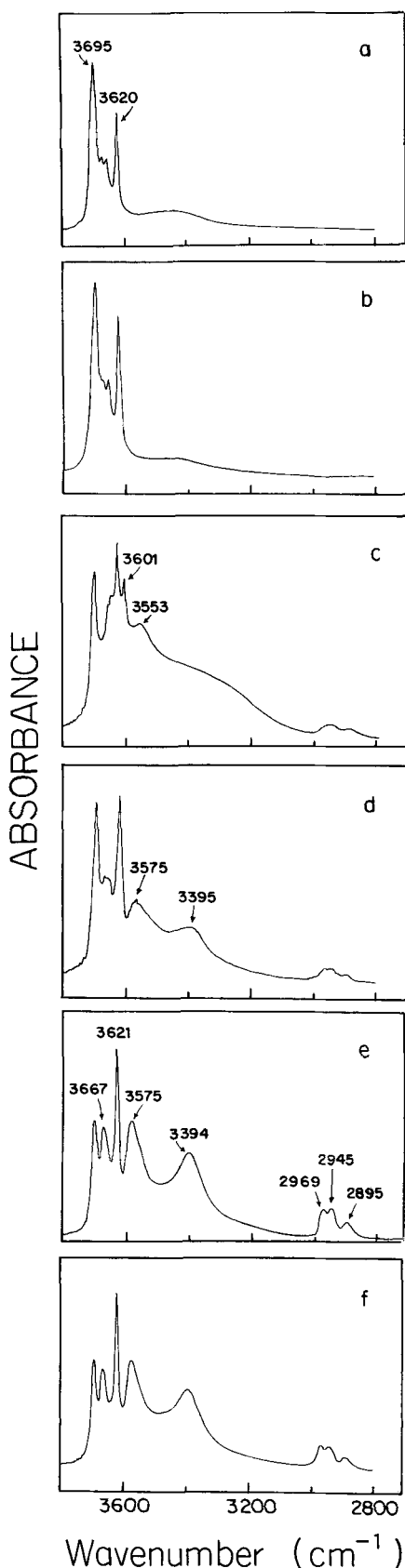


Figure 3. XRD patterns 4–14 degrees 2θ before (—) and after (---) heating at 200°C for one hour of: (a) kaolinite starting material; (b) Kao-EG 10.8 Å; (c) Kao-EG 9.4 Å.

In an attempt to better understand what phases are formed once the volatile component (<200°C) is expelled, an experiment was performed whereby small portions (100 mg) of kaolinite, Kao-EG 10.8 Å and Kao-EG 9.4 Å were heated in a furnace at 200°C for one hour, followed by XRD and infrared analysis before and after thermal treatment. These results are shown in Figures 3 and 4. From these figures, it is clear that whereas kaolinite and Kao-EG 9.4 Å change little upon thermal treatment, Kao-EG 10.8 Å is transformed into Kao-EG 9.4 Å and kaolinite.

Powder XRD. Figures 1a–1f show the XRD pattern of the various products formed by varying the water con-



tent of the reaction media. In Figures 1b (0% water content), 1e and 1f (5% and 10% water content respectively) the XRD patterns show a superposition of two separate phases. In the case of Figure 1b there is the Kao-EG 9.4 Å phase superimposed on the residual kaolinite phase. Both the d_{002} ($18.9^\circ 2\theta$) and the d_{003} ($28.5^\circ 2\theta$) peaks are clearly observable in addition to the intense d_{001} peak ($9.3^\circ 2\theta$) thus indicating a relatively low stacking disorder. The same can also be said for the principal Kao-EG 10.8 Å phase in Figure 1f, where the d_{001} ($8.2^\circ 2\theta$), d_{002} ($16.4^\circ 2\theta$) and d_{003} ($24.7^\circ 2\theta$) reflections can be identified. Here, the d_{003} reflection overlaps somewhat with the d_{002} ($24.9^\circ 2\theta$) reflection of the residual kaolinite.

In Figures 3a–c, the 4– $14^\circ 2\theta$ XRD patterns illustrate the effects of heating at 200°C on the Kao-EG 9.4 Å and Kao-EG 10.8 Å phases. There is no change in the d_{001} peak of kaolinite upon heating at 200°C (Figure 3a). Both the position ($d = 7.14$ Å), and the peak width ($0.16^\circ 2\theta$) remain constant upon heating.

In the case of Kao-EG 10.8 Å (from trial 4), it was found that thermal treatment caused significant changes in the XRD pattern (Figure 3b). The peak at $d = 10.75$ Å ($8.2^\circ 2\theta$) was eliminated upon heating at 200°C and instead, the peak at $d = 9.4$ Å ($9.4^\circ 2\theta$) was drastically increased in relative intensity from 2.1 to 100.0. The relative intensity of the residual kaolinite d_{001} peak at $d = 7.14$ Å ($12.4^\circ 2\theta$) also increased in relative intensity from 4.6 to 17.5 upon heating at 200°C.

For Kao-EG 9.4 Å (from trial 1), heating at 200°C caused a slight shift in the d_{001} peak position from 9.52 Å ($9.3^\circ 2\theta$) to 9.39 Å ($9.4^\circ 2\theta$), but the main difference was the reduction in peak width from 0.36 to $0.24^\circ 2\theta$.

Infrared spectroscopy. Figures 4a–4f show the effects of heating to 200°C on the C-H and O-H stretching regions of the infrared spectrum. The characteristic O-H stretching pattern of the parent kaolinite remained unchanged upon heating (Figures 4a and 4b). The 3695, 3669, and 3652 cm^{-1} peaks have been assigned to the interlamellar surface O-H stretching vibrations of the Al-OH surface of kaolinite (Johnston *et al* 1984; Rouxhet *et al* 1977). The 3620 cm^{-1} peak is the O-H stretching frequency corresponding to the internal hydroxyl group of the kaolinite.

Upon formation of Kao-EG 10.8 Å as the main phase one sees a corresponding change in the infrared O-H and C-H stretching region (Figure 4c). The 3620 cm^{-1} peak corresponding to the O-H stretching frequency of the internal hydroxyls of kaolinite remains unchanged since, plausibly, modification takes place in the inter-

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Figure 4. FTIR spectra of the O-H and C-H stretching region for: (a) kaolinite; (b) kaolinite after heating at 200°C 1 h; (c) Kao-EG 10.8 Å (trial 4); (d) Kao-EG 10.8 Å (trial 4) after heating at 200°C 1 h; (e) Kao-EG 9.4 Å (trial 1); (f) Kao-EG 9.4 Å (trial 1) after heating at 200°C 1 h.

layers and not in the structure itself. The 3695 cm^{-1} peak decreased in intensity as a series of ill defined peaks at 3651 , 3640 , 3601 and 3553 appeared, superimposed on a broad hydrogen bonded OH stretching beginning at 3100 cm^{-1} . In addition, two broad, low intensity peaks in the C-H stretching region appeared at about 2880 and 2950 cm^{-1} . This corresponds roughly to the symmetric and antisymmetric C-H stretching bands of neat ethylene glycol (2874 and 2941 cm^{-1}). It is also noteworthy that there is almost no absorption around 1650 cm^{-1} (Figure 5), thus ruling out the possibility of significant amounts of water being intercalated into the interlamellar space of kaolinite since this is the area where the bending deformation $\delta(\text{H-O-H})$ of water occurs.

Upon heating at 200°C , the infrared pattern of the Kao-EG 10.8 \AA product changed significantly (Figure 4d), in accordance with what was seen by XRD (Figure 3b). Both IR and XRD confirmed that the Kao-EG 10.8 \AA phase had been partially converted to the Kao-EG 9.4 \AA phase. This can be seen by the similarity between the infrared spectra in Figure 4d and that of the Kao-EG 9.4 \AA product in Figures 4e and 4f. In contrast to the Kao-EG 10.8 \AA product, the infrared pattern of the Kao-EG 9.4 \AA product remains essentially unchanged upon heat treatment at 200°C (Figures 4e and 4f).

For the Kao-EG 9.4 \AA product, there exists five distinct OH stretching frequencies. The 3620 cm^{-1} peak remains unchanged since the internal structural hydroxyl group of kaolinite is removed from the probable sites of modification. The 3695 cm^{-1} and the 3667 cm^{-1} peaks are due to the interlamellar surface hydroxyls of the Al-OH kaolinite sheet. The peak at 3575 cm^{-1} is proposed to be due to the hydrogen bonded component of the interlamellar surface hydroxyls of kaolinite. This hydrogen bonding involves the ethylene glycol moiety, which in turn has a hydrogen bonded O-H stretching frequency at still lower energy at 3394 cm^{-1} .

As for the C-H stretching region, there now appears to be three distinct C-H stretching bands at 2895 cm^{-1} , 2945 cm^{-1} and 2969 cm^{-1} . This contrasts with the situation for neat ethylene glycol and the Kao-EG 10.8 \AA product (Figure 3c) where only two bands indicative of the symmetric and antisymmetric C-H stretching modes were observed.

The alumino-silicate framework of kaolinite absorbs strongly in the region $1000\text{--}1200\text{ cm}^{-1}$, and neat ethylene glycol is characterized by two absorption bands, due to the C-C-O stretchings at 1087 and 1044 cm^{-1} . In the case of three aluminum alkoxides, the Al-O-C linkage was characterized by the presence of a band in the region 1030 to 1070 cm^{-1} (Guertin *et al* 1956). The presence of a band at 1100 cm^{-1} was mentioned recently as being characteristic of this linkage in the case of a barium aluminate glycolate (Herreros *et al*

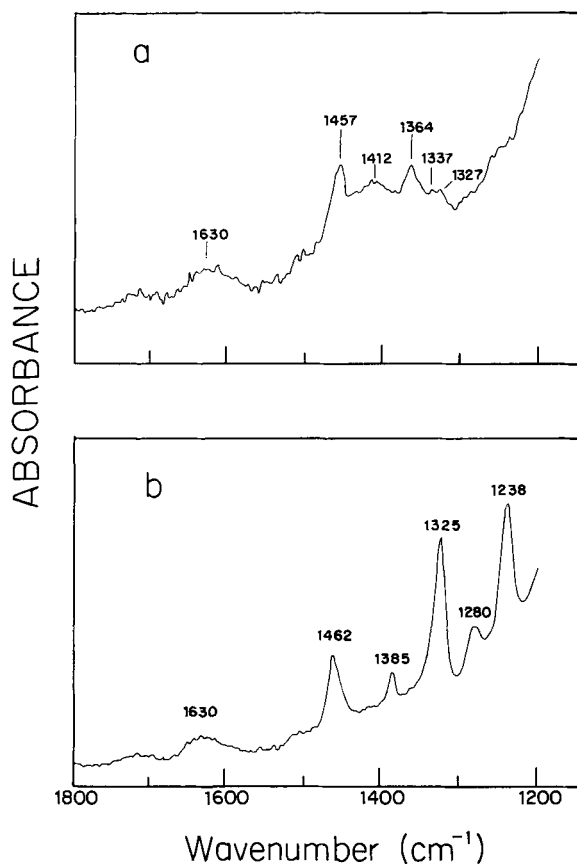


Figure 5. FTIR spectra ($1200\text{--}1800\text{ cm}^{-1}$) of: (a) Kao-EG 10.8 \AA ; (b) Kao-EG 9.4 \AA .

1994). In both Kao-EG 9.4 \AA and Kao-EG 10.8 \AA , the region $1000\text{--}1200\text{ cm}^{-1}$ is strongly modified, showing, in first approximation, the superposition of the spectra of kaolinite and ethylene glycol.

In general, the absorption bands are narrower for the 9.4 \AA phase compared to the 10.8 \AA one, showing a strong rigidification of the organic units in Kao-EG 9.4 \AA . This is particularly striking in the region of the CH_2 deformation bands, between 1200 and 1500 cm^{-1} (Figure 5). Five bands of weak (w) or very weak (vw) intensity can be clearly identified on the Kao-EG 9.4 \AA spectrum, at 1238 (w), 1280 (vw), 1325 (w), 1385 (vw) and 1462 (w) cm^{-1} (Figure 5b). This region is diagnostic of the conformation, gauche or trans, of the ethyleneoxy, O- $\text{CH}_2\text{-CH}_2\text{-O}$, groups. The clear presence of a band at 1325 cm^{-1} suggests the trans conformation, since in previous work, involving polyethyleneoxide (PEO) chains, the lack of a band at 1322 cm^{-1} was assumed to be diagnostic of ethyleneoxy units in the gauche conformation (Aranda and Ruiz-Hitzky 1992). This was assumed on the basis of the vibrational spectra of PEO·Hg salt complexes, whose structure is known from X-ray analysis to be in a planar zig-zag conformation in which the ethyleneoxy groups are in

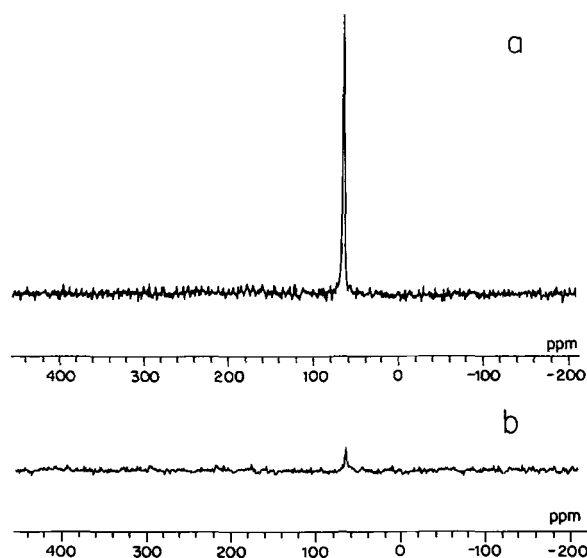


Figure 6. (a) ^{13}C CP/MAS and (b) ^{13}C DD/MAS (dephasing period = 40 μs) NMR spectra (75.37 MHz) of Kao-EG 9.4 Å.

trans and gauche conformations. The presence of a band at 1322 cm^{-1} was attributed to the trans conformation of the $-\text{O}-(\text{CH}_2-\text{CH}_2)-\text{O}-$ unit.

^{13}C NMR. Figure 6 shows the ^{13}C CP/MAS and DD/MAS NMR spectra of Kao-EG 9.4 Å prepared in the conditions of trial 1 of Table 1. A relatively broad signal ($\nu_{1/2} \approx 190\text{ Hz}$) is observed at 64 ppm. The dipolar dephasing experiment eliminates almost completely the signal, showing the presence of very rigid organic units.

DISCUSSION

The Kao-EG 10.8 Å phase has been assigned as the ethylene glycol intercalate of kaolinite (Camazano and Garcia 1966; Range *et al* 1969), whereas the Kao-EG 9.4 Å phase was described as an ethylene glycol grafted organo-kaolinite with the ethylene glycol units attached via Al-O-C bonds (Tunney and Detellier 1993). From the series of experiments summarized in Table 1, it appears that the concentration of water plays an intricate role in determining the product distribution. A surface condensation reaction between aluminol and alcohol groups would yield an S-O-R surface ether and water. One would expect that excess water would drive the reaction towards the unmodified hydroxylated surface and free alcohol whereas a low concentration of water should favor the formation of the grafted surface ether. Assuming that the forward reaction is endothermic, one would also expect that heating would drive the reaction towards the formation of the surface ether species. This simplistic model therefore, can rationalize the roles of water content and of heat in determining which type of ethylene glycol organo-kaolinite is formed. Moreover, the 9.4 Å phase resulting from

the synthesis in the presence of a low percentage of water (trials 2 and 3 of Table 1) was slowly (month time scale) converted into the 10.8 Å phase.

One would expect the surface ether linkage (Al-O-R) to be susceptible to water hydrolysis once formed in Kao-EG 9.4 Å. This is apparently not the case since it was found that even upon refluxing the predominant Kao-EG 9.4 Å product of trial 1 in 100% water for 20 h, almost no decomposition of the Kao-EG 9.4 Å phase could be detected as judged by comparing the O-H stretching region of the infrared spectra before and after refluxing in water. Once formed, the Kao-EG 9.4 Å phase exhibits remarkable resistance to water hydrolysis. Similarly it was found that a refluxing 90:10 mixture of ethylene glycol : water was also unable to cause significant hydrolysis of the Kao-EG 9.4 Å phase to yield either the Kao-EG 10.8 Å ethylene glycol intercalate or the 7.2 Å parent kaolinite. A refluxing mixture of approximately 5% water in DMSO was however able to cause decomposition of the Kao-EG 9.4 Å phase. This mixture could hydrolyze and displace the interlamellar ethylene glycol units to yield as the main phase the 11.2 Å intercalate Kao-DMSO as well as residual Kao-EG 9.4 Å and 7.2 Å kaolinite.

Upon formation of the Kao-EG 9.4 Å phase, the interlamellar spaces of this organo-kaolinite become relatively inaccessible to water and thus water hydrolysis, unless accompanied by a strongly penetrating media such as DMSO capable of prying open the layers. In comparison, it was possible to deintercalate Kao-EG 10.8 Å by washing with water overnight. After filtering and air drying the product reverted either to a collapsed 7.2 Å kaolinite or to an 8.4 Å hydrate (Tunney and Detellier 1994).

However, using more drastic conditions, namely reacting the product in water in an autoclave at 200°C for 72 h, a partial decomposition could be observed. The recovered solid phase consisted of a mixture of kaolinite and of the starting material, as shown by X-ray data. The relative proportion of kaolinite was greatly enhanced with respect to the Kao-EG 9.4 Å starting material. The solution (supernatant) contained only ethylene glycol as organic material. One could not detect by ^{13}C NMR any trace of any other organic material. This result rules out the possibility of the formation and the presence of oligoethyleneglycols or of polyethyleneglycol in the interlayer spaces of kaolinite. Moreover, no signals around 72 ppm, expected for ether carbons, or in the range 69–72 ppm, as recently observed for intercalates of poly(ethylene oxide) in hectorite (Aranda and Ruiz-Hitzky 1992), could be detected on the ^{13}C NMR CPMAS spectrum of Kao-EG 9.4 Å. At least two other evidences point to the lack of oligomerization or polymerization of EG: (a) the DSC of Kao-EG 9.4 Å shows an endothermic weight loss in the range $300\text{--}400^\circ\text{C}$ (both under N_2 or air flow), while the di-, tri-, and tetraethylene glycol intercalates

all give an exothermic event; (b) These oligoethylene-glycol intercalates are characterized by d_{001} spacings around 11.0 Å, much higher than the observed 9.4 Å.

Only one relatively broad signal could be observed on the ^{13}C NMR spectrum. Inoue *et al* (1991a) have recently published the ^{13}C CP/MAS NMR spectra of the products obtained by the reaction of $\text{Al}(\text{OPr}^i)_3$ in ethylene glycol and other diols. The ^{13}C chemical shifts of the oxygenated carbons of the products (containing C-O-Al bonds) were all around 60 ppm, close to the methine carbons resonances of $\text{Al}(\text{OPr}^i)_3$, in the solid state (Inoue *et al* 1991a) and in solution (63.4 ppm) (Akitt and Duncan 1974). These data show that the effects on the ^{13}C NMR chemical shifts of an aluminate (^{13}C -O-Al) or of an hydroxyl (^{13}C -O-H) substituents are unfortunately very similar. If the ^{13}C NMR spectra show unambiguously the complete replacement of DMSO molecules by ethylene glycol, as well as the absence of any oligomerization or polymerization products, it does not provide definite evidence for the formation of an Al-O-C linkage. However, it does not rule out the hypothesis that "one end of EG is grafted to form an Al-O-C bond, while the remaining OH group is keyed into the (-Si-O-)₆ macro-ring of the silicate side by hydrogen bonding" (Tunney and Dettellier 1993), which is in good agreement with the other spectroscopic and chemical observations.

On the basis of the TGA data (percentage of weight loss of water and organics to form metakaolinite $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), the following formula can be calculated: $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_{3.2}(\text{OCH}_2\text{CH}_2\text{OH})_{0.8}$. This is in good agreement with X-ray fluorescence data (SiO_2 : calc: 40.9%; found: 39.7%; Al_2O_3 : calc: 34.8%; found: 34.4%) and chemical analysis data (C: calc: 6.55%; found: 6.51%; H: calc: 2.46%; found: 2.48%).

However, at this point, because of the lack of definite evidence for the presence of an Al-O-C linkage, one can not completely rule out the hypothesis of the formation of a 9.4 Å phase, characterized by strongly rigid ethylene glycol intercalates in the trans conformation with both hydroxyl groups keyed in the kaolinite structure, respectively on/in the aluminate and the silicate layers.

CONCLUSION

A new phase of a kaolinite intercalate of ethylene glycol was synthesized by refluxing the kaolinite-DMSO intercalate in dry ethylene glycol. It was characterized by FTIR, TGA/DSC, NMR and X-Ray techniques. This material (Kao-EG 9.4 Å), characterized by a d_{001} of 9.4 Å, is resistant to decomposition by hydrolysis in pure water and ethylene glycol: water (90:10). Its formation depends crucially upon the water content of the ethylene glycol used in the synthesis procedure. It is probable that ethylene glycol is grafted on the kaolinite interlamellar surfaces through Al-O-C bonds.

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