Grafted organic derivatives of kaolinite: II. Intercalation of primary n-alkylamines and delamination

J. E. F. C. GARDOLINSKI* AND G. LAGALY

Institute of Inorganic Chemistry, University of Kiel, D-24098, Kiel, Germany

ABSTRACT: Kaolinite was intercalated with n-hexylamine, n-octadecylamine and n-docosanamine, using methanol-kaolinite as the precursor. The intercalation compound with n-docosanamine presented the largest basal spacing for a kaolinite derivative thus far reported (64.2 Å). Five grafted derivatives of kaolinite were directly intercalated with n-hexyl- and n-octadecylamine. During intercalation, the grafted molecules rearrange from parallel to perpendicular orientation to the kaolinite surface, in order to maximize the interaction with the amine and minimize the interlayer expansion needed. The octadecylamine intercalation compounds were delaminated in toluene, accompanied by the deintercalation of the amine molecules. Thin kaolinite particles rolled into a halloysite-like morphology, but forming much smaller tubes, some of which possibly consist of single kaolinite layers. The delamination was more efficient with the grafted kaolinites than with raw kaolinite.

Delamination and exfoliation are terms used in modern literature, unfortunately often neglecting to distinguish between them. When dealing with clay minerals (and many other layered materials), a clear distinction between the two terms is easily established. Exfoliation is defined as the decomposition of large aggregates (booklets) into smaller particles. Delamination denotes the process of separation of the individual layers of the particles.

Exfoliation of kaolinite is an important industrial procedure, e.g. it influences the rheological properties of dispersions used in the ceramic industry and the coating properties of the kaolins used in the paper industry. Exfoliated kaolins usually have a higher aggregate value than the raw material, and the exfoliation process can increase the usability of

reserves otherwise unsuited for many applications (Jasmund & Lagaly, 1993).

Industrial (and experimental) exfoliation of kaolins is obtained by mechanical methods (Tari *et al.*, 1988; Jasmund & Lagaly, 1993; Maxwell & Malla, 1999), but chemical approaches have also been described (Lahav, 1990; Tsunematsu *et al.*, 1992; Maxwell & Malla, 1999; Tsunematsu & Tateyama; 1999; Gardolinski *et al.*, 2001; Triplehorn *et al.*, 2002). These processes are based on the intercalation of molecules such as urea or potassium acetate, concomitant (or not) with mechanical treatments.

True delamination of kaolinite into stable aluminosilicate monolayers has not yet been achieved. The delamination process previously described by Lahav (1990) with the alleged formation of single layers by combined dimethyl sulphoxide and ammonium fluoride treatment was shown to be based on misinterpreted data. In fact, the amount of finer fractions was increased insignificantly and only platy particles were

* E-mail: jegardol@yahoo.com

formed (Chekin, 1992). These remarks were corroborated by later results on particle-size and microscopic analysis of the kaolinite treated by Lahav's method (Gardolinski, unpublished data).

The chemical exfoliation using ammonium acetate (Weiss & Russow, 1963) or potassium acetate (Singh & Mackinnon, 1996), however, has been studied in detail. Many (>30) cycles of intercalation/deintercalation (washing with water) exfoliated the particles forming thinner lamellae, which eventually curled to halloysite-like tubes and/ or polygonal spirals. Briefly described were similar results where a kaolinite, previously intercalated with n-octylamine, was washed with ethyl ether (Poyato-Ferrera *et al.*, 1977).

The microscale morphology of the tubes and polygonal spirals obtained by the intercalation/ deintercalation cycles of kaolinite with potassium acetate was shown to be indistinguishable from natural halloysite, presenting a highly disordered structure with intercalated water (Singh & Mackinnon, 1996). It was shown that kaolinite layers curl to compensate the lateral misfit between the octahedral and tetrahedral sheets when the interlayer hydrogen bonds are sufficiently weakened. In planar particles, the misfit is compensated by rotation of the SiO_4 tetrahedra. The curling mechanism is energetically more favourable than tetrahedral rotation, but can only proceed in sufficiently thin particles with a highly disordered structure and strongly weakened inter-layer hydrogen bonds, as in the case of potassium or ammonium acetate treatments (Singh, 1996). The rolling of the octylamine-intercalated kaolinite after washing with ether can be interpreted in the same way. The large basal spacing of the intercalate impedes the formation of hydrogen bonds between the kaolinite layers.

The rolling of very thin kaolinite particles poses an obstacle to the further separation of the layers in order to obtain fully delaminated samples, as the layers will tend to adhere together, stabilized as tubes and spirals. A more efficient method is needed to increase the degree of delamination of kaolinite.

It was the aim of this work to investigate the delamination of kaolinite using an optimized method based on intercalation of long-chain amines and washing in an organic medium, as well as to determine how the interlayer grafting of organic molecules into kaolinite would influence this delamination process.

EXPERIMENTAL

Materials

A well crystallized kaolinite ('SPS', Hinckley crystallinity index = 1.25) supplied by the English Clays Lovering Pochin & Co. (now Imerys Minerals Ltd - Cornwall, UK) was used as received. DMSO, alcohols, diols, glycol mono-ethers, n-hexylamine and n-octadecylamine were obtained from Sigma-Aldrich (Germany) in purities of at least 98% and used without further treatment. The n-octadecyl-amine contained ~10% (w/w) n-hexadecylamine. n-docosanamine (behenylamine, 22 carbon atoms) was obtained from Lachat Biochemical Company (Chicago, USA).

Synthesis of the grafted kaolinites

Kaolinite was grafted with 1,3-butanediol, di(ethylene glycol) methyl ether, di(ethylene glycol) 2-ethyl-hexyl ether, tri(propylene glycol) butyl ether, 1-pentanol and 1-heptanol. The synthesis of these derivatives is discussed in an accompanying paper (Gardolinski & Lagaly, 2005).

Intercalation of amines

Grafted kaolinites were intercalated with n-hexyl-amine dispersing ~5 g of kaolinite in ~50 ml of amine in closed vessels for 24 h. The dispersions were centrifuged and the sediments redispersed in the same volume of fresh amine. The dispersions were stirred for another 24 h and then centrifuged. The moist products were kept in closed vessels for further use.

n-octadecylamine was intercalated by displace-ment of the hexylamine previously intercalated. Typically, ~1 g of hexylamine-intercalated grafted kaolinite was added to ~20 ml of melted amine (80−90ºC) and kept under stirring for 2 days. The dispersion was centrifuged while hot, and the process was repeated with fresh amine. This final product was centrifuged, cooled and manually ground to a fine powder.

Intercalation of amines into ungrafted kaolinite was performed by the same procedure, but using freshly prepared methanol-kaolinite as precursor. The methanol-kaolinite (Raythatha & Lipsicas, 1985; Komori *et al.*, 1998) was prepared by repeated washing of dimethyl sulphoxide-kaolinite (Weiss *et al.*, 1966; Olejnik *et al.*, 1968) with methanol.
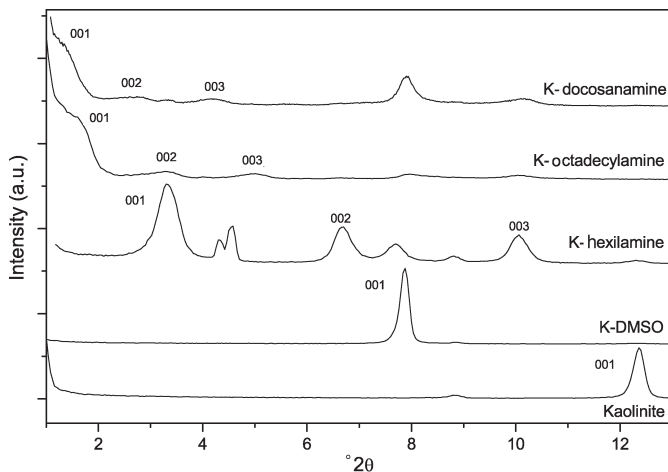
FIG. 1. XRD patterns of the intercalation products obtained from non-grafted kaolinite.

Delamination

Grafted and pristine kaolinites intercalated with n-octadecylamine were used for the delamination experiments. Samples of the intercalation compounds (typically ~0.5 g) were slowly added to ~50 ml of toluene in a jacketed beaker and kept under intensive magnetic stirring. The dispersions were sonicated for 2×5 min (5 min pause, UP200S equipment, Dr Hielscher GmbH, Germany, frequency 24 kHz, power output 200 W, cylindrical titanium probe with 7 mm diameter). The temperature of the system was kept below 25ºC by circulation of fresh water in the beaker jacket.

After this treatment, the dispersions were centrifuged at 60000 g for 30 min. The separated products were dispersed in 50 ml of toluene and kept in agitation for 20 h. These products were centrifuged and washed three more times with 50 ml of ethyl ether (~20 h for each washing step) and then dried at 60ºC for 24 h.

Methods

X-ray powder diffraction (XRD) patterns were recorded using a Philips D5000 diffractometer (Cu-$K\alpha$ radiation, count time = 3.5 s, step size = 0.04º). The basal spacings (d_L) were calculated from the basal reflection of the highest detectable order. The morphological studies (micrographs) were performed using a Philips EM 400T transmission electron microscope operated at 100 V. The microscopy probes of the delaminated kaolinites were prepared by adding a small drop of the ether dispersions onto a Lacey carbon film-coated copper grid and allowed to dry in air.

RESULTS AND DISCUSSION

XRD analysis

The dimethyl sulphoxide-kaolinite (K-DMSO, Fig. 1) showed the typical basal spacing of 11.2 Å

TABLE 1. Basal spacings (d_L) and literature values (d_L(lit)) of the intercalation compounds of kaolinite.

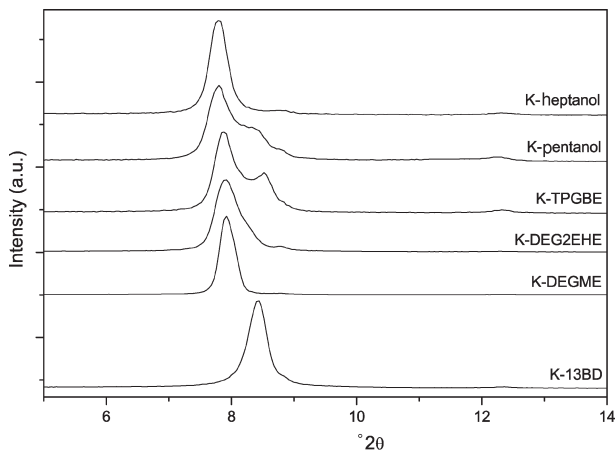| Guest molecule	d_L (Å)	d_L(lit) (Å)
DMSO	11.2	11.2 (Weiss *et al.*, 1966; Olejnik *et al.*, 1968)
Hexilamine	26.6	26.9 Å (Komori *et al.*, 1999) 25.3 Å (Weiss *et al.*, 1966)
Octadecylamine	53.2	57.5 Å (Komori *et al.*, 1999) ~58.0 Å (Weiss *et al.*, 1966)
Docosanamine	64.2	–

FIG. 2. XRD patterns of the grafted kaolinites.

(Weiss *et al.*, 1966; Olejnik *et al.*, 1968). The hexylamine-kaolinite had a basal spacing of 26.6 Å, similar to the values of 26.9 Å (Komori *et al.*, 1999) and 25.3 Å (Weiss *et al.*, 1966) previously reported. The basal spacing of the octadecylamine-kaolinite (53.2 Å) was slightly smaller than the reported values of 57.5 Å (Komori *et al.*, 1999) and ~58.0 Å (Weiss *et al.*, 1966). The basal spacing of 64.2 Å of the intercalation compound with n-docosanamine (not previously described) is, to the best of our knowledge, the largest spacing reported thus far for a kaolinite intercalation compound (Table 1).

These values indicate that the alkyl chains are fully stretched (all-*trans* conformation) and perpendicular to the basal plane surface, arranged in a bilayer between the kaolinite layers. The amino groups interact at one side with the interlayer hydroxyl groups, and on the other side with the silica sheet (Weiss *et al.*, 1966; Komori *et al.*,

1999). The smaller basal spacing obtained with n-octadecylamine in comparison to the literature values is probably due to contamination of the amine with n-hexadecylamine (Weiss *et al.*, 1966) and/or formation of kinks (Lagaly *et al.*, 1975).

Figure 2 presents the XRD patterns of the grafted kaolinites. The basal spacings of these compounds are listed in Table 2. A detailed description is given in an accompanying paper (Gardolinski & Lagaly, 2005). The basal spacings of the grafted kaolinites intercalated with n-hexylamine (Table 3) are slightly smaller (<1 Å) than that of raw kaolinite intercalated with the same amine. The compounds intercalated with n-octadecylamine (Table 3, Fig. 3) had basal spacings that were larger by 2−3 Å than with the octadecylamine-kaolinite. Considering the uncertainty in the determination of the basal spacings from the broadened reflections in the low-2θ region, one can assume that the amine molecules in the grafted kaolinites are arranged

TABLE 2. Basal spacings (d_L) of the grafted kaolinites.

Grafted molecule	Product	d_L (Å)
1,3-butanediol	K-13BD	11.3
Di(ethylene glycol) methyl ether	K-DEGME	11.0
Di(ethylene glycol) 2-ethylhexyl ether	K-DEG2EHE	11.3
Tri(propylene glycol) butyl ether	K-TPGBE	11.3 (70%) 10.3 (30%)
1-pentanol	K-pentanol	11.3 (75%) 10.3 (25%)
1-heptanol	K-heptanol	11.3

TABLE 3. Basal spacings (d_L) of the grafted kaolinites intercalated with n-hexyl and n-octadecylamine.

Compound	d_L n-hexylamine (Å)	d_L n-octadecylamine (Å)
K-13BD	25.7	55.1
K-DEGME	25.7	56.6
K-DEG2EHE	26.2	55.5
K-TPGBE	26.4	54.7
K-pentanol	26.0	56.1
K-heptanol	26.5	55.8

such that the amino groups interact with the inner-surface hydroxyl groups in a similar way as in the ungrafted kaolinite. During intercalation, the grafted molecules must have changed from an almost parallel orientation to the basal plane surfaces to a perpendicular orientation (Fig. 4). In this arrangement, the interaction between the alkyl chains of grafted molecule and amine is maximized and the basal expansion needed to accommodate the amine bilayer is kept to a minimum. This explains the very small differences between the basal spacing of the amine-intercalated grafted and raw kaolinites.

As shown by the diffraction patterns (Fig. 3), the intercalation reactions did not proceed quantitatively, as reflections of the grafted kaolinites are still identifiable. Noteworthy is the fact that the amines are directly intercalated into the grafted kaolinites, but not into raw kaolinite or K-DMSO (Komori *et al.*, 1999). The broadened reflections of the intercalation compounds show that the inter-

calation of the amine bilayer considerably reduces the crystalline order of the kaolinite structure.

Figure 5 shows the XRD patterns of the amine-intercalated kaolinites (grafted and ungrafted) after the deintercalation and washing procedures. The ungrafted kaolinite is deintercalated almost quantitatively, as shown by a very weak broadened reflection at a low 2θ value that is attributed to remnants of intercalated amine, probably as a highly inhomogeneous interstratified phase. The reflection at d_L = 8.7 Å is attributed to the dry kaolinite-methanol intercalation compound (Komori *et al.*, 1998) and the small reflection at d_L = 11.2 Å is due to the K-DMSO, both phases remnants of the precursor kaolinites. The reflection at d_L = 10.0 Å comes from the mica present in the original kaolinite sample. Due to the lower crystallinity of the final product, the mica, which is not affected by the process, is now easily recognized.

The XRD patterns of the delaminated grafted kaolinites show many similarities to those of the delaminated raw (ungrafted) kaolinite. The amine molecules are deintercalated, and the original basal spacings of the grafted kaolinites are recovered. A weak broadened reflection at a low 2θ value is attributed to an interstratified phase, as in the deintercalated raw kaolinite. The derivatives from DEGME and heptanol present a better defined reflection at $d_L \approx 40$ Å. It is supposed that the particles remaining intercalated with octadecylamine present a different arrangement for the alkyl chains, probably with the formation of kinks (Lagaly *et al.*, 1975) or by partially squeezing the alkyl chains out of the interlayer spaces (Poyato-Ferrera *et al.*, 1977).
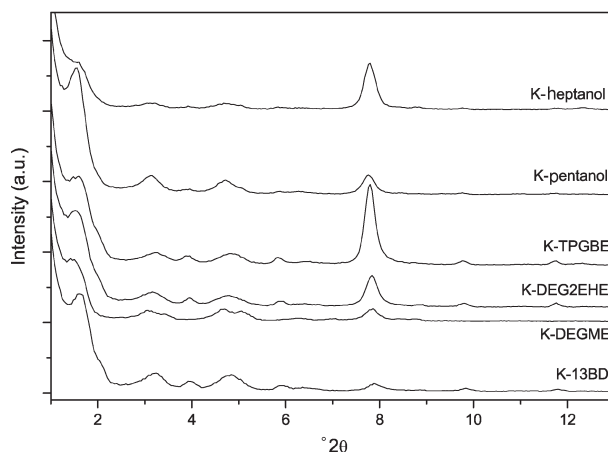

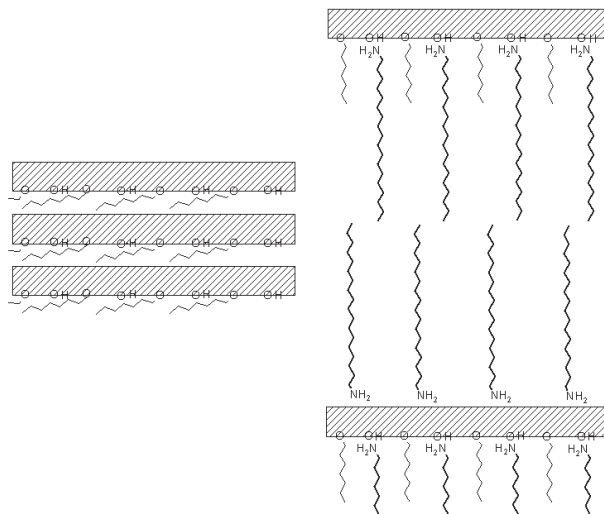FIG. 3. XRD patterns of grafted kaolinites intercalated with n-octadecylamine.

FIG. 4. Schematic view of the proposed disposition of the grafted molecules in K-heptanol before and after intercalation with n-octadecylamine (not to scale).

Deintercalation of the derivative from 1,3-butanediol does not recover the original basal spacing (11.3 Å), but produced a weak reflection at 10.7 Å. This compound also shows a much smaller degree of crystallinity in comparison to the other deintercalated compounds, possibly indicating extensive delamination of the sample.

Morphology

Any conclusions about the success of the delamination process must be based on the morphological analysis of the deintercalated products. The raw, untreated kaolinite is composed of platy, euhedral particles with typical pseudo-hexagonal morphology (Fig. 6). After the intercalation/deintercalation steps (Fig. 7), the sample still presents some thicker particles, but the bulk of the sample is composed of thin plates and elongated units. At a higher magnification, the elongated units are recognized as thin kaolinite particles in the form of hollow tubes. As expected, the deintercalation process separates very thin lamellae from the kaolinite particles. These lamellae curl to form the observed tubes. The smallest tubes in the sample had an external diameter of ~25 nm, which is
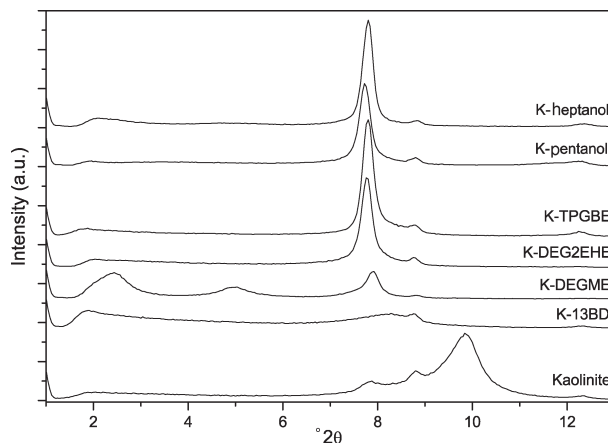

FIG. 5. XRD patterns of kaolinite and grafted derivatives after deintercalation.
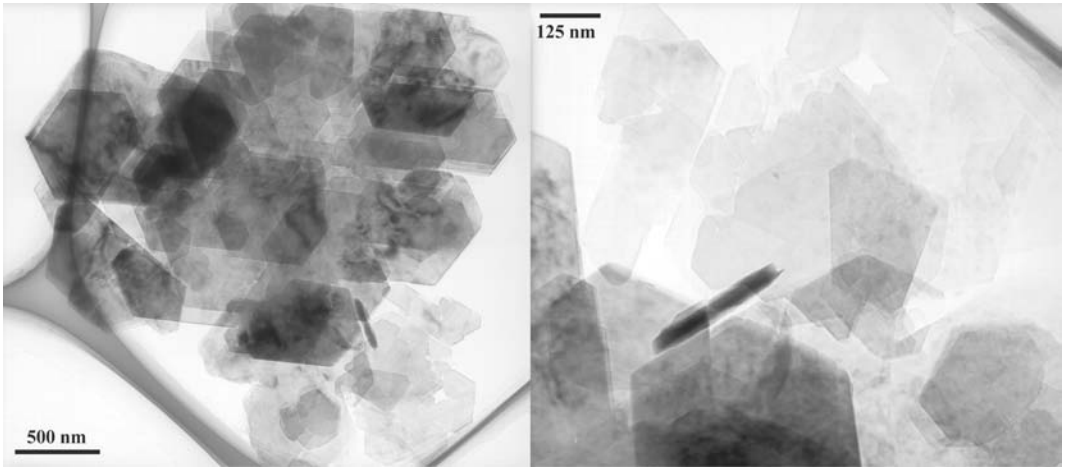
FIG. 6. TEM images of raw kaolinite.

consistent with the calculated minimum internal diameter for a tube formed by a single kaolinite layer (Bates *et al.*, 1950).

The samples obtained by deintercalation of the grafted kaolinites showed a more extensive degree of rolling than the samples derived from raw kaolinite. They contained some kaolinite particles with recognizable pseudo-hexagonal morphology, some damaged particles, thin plates and a large number of tubes (Figs 8, 9). All tubes formed from the different grafted kaolinites were morphologically similar. The minimum external diameter of the tubes was also ~25 nm. The derivative from 1,3-butanediol showed only very small amounts of platy particles, being composed almost exclusively of tubes and some curled thin plates.

Two essential factors contributed to the higher degree of rolling of the grafted derivatives. The organically modified interlayer surface can interact more efficiently with toluene than the original ungrafted surface. In addition, the intercalation of amines formed products with higher stacking disorder, indicated by the broadened reflections of the XRD patterns, which is a key parameter in the separation of the layers (Singh & Mackinnon, 1996; Singh, 1996).

To date it has been accepted that the hydration of the kaolinite interlayer spaces is an essential requirement to separate and curl the layers, because it generates the higher degree of disorder needed to weaken the interlayer hydrogen bonds (Singh, 1996; Singh & Mackinnon, 1996). The
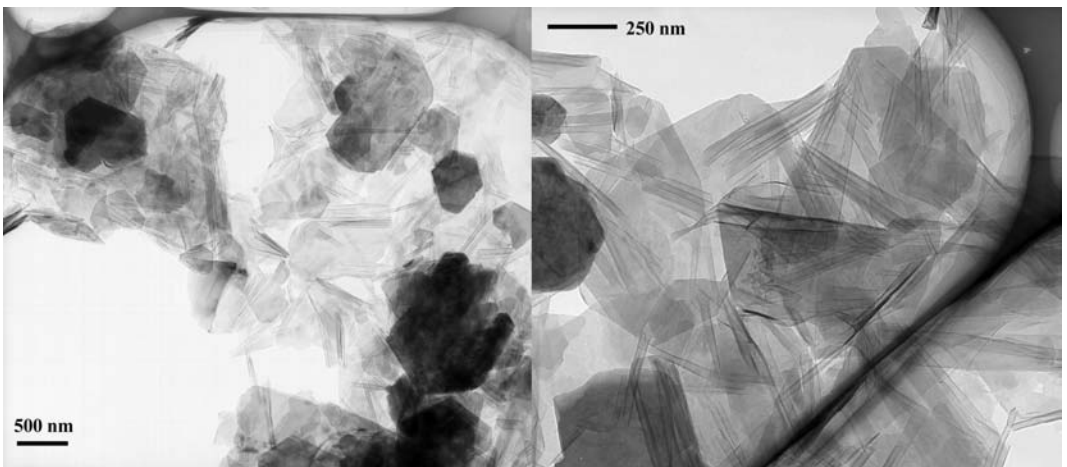

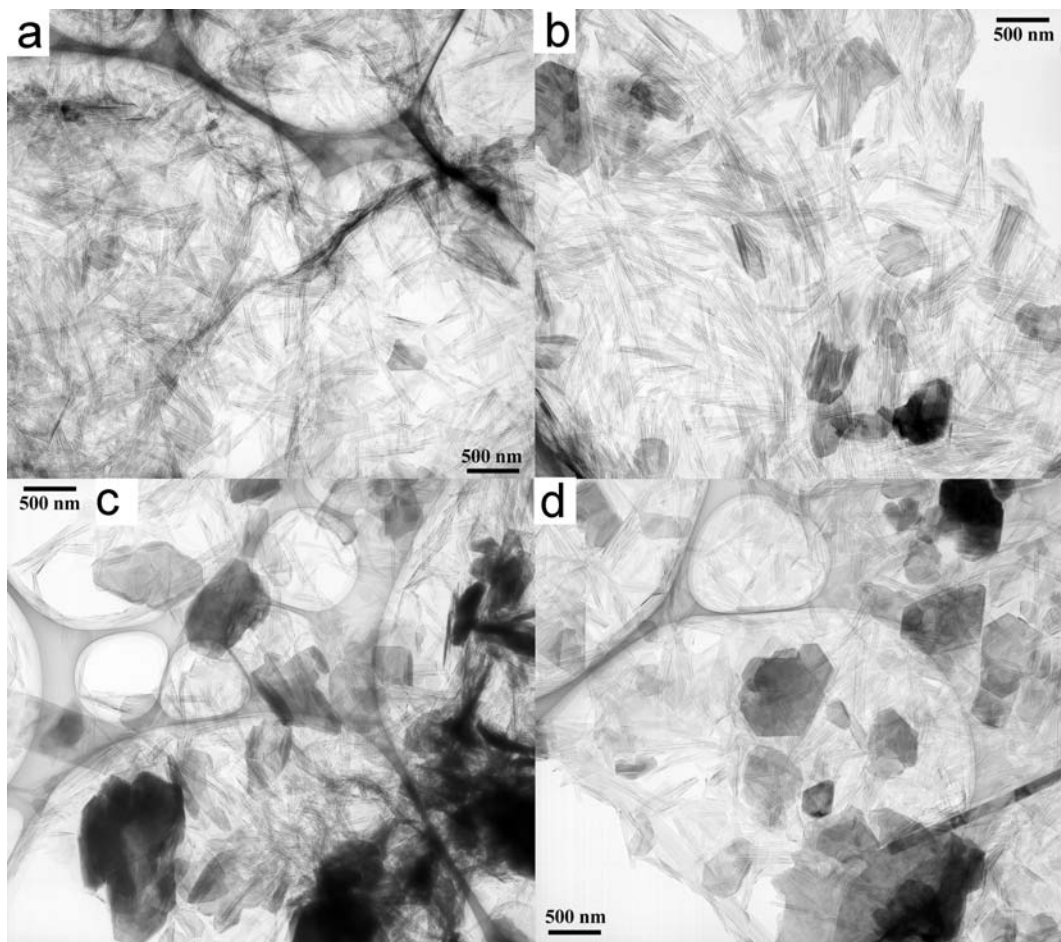FIG. 7. TEM images of the deintercalated kaolinite.

FIG. 8. TEM images of the deintercalated kaolinites grafted with (a) 1,3-butanediol, (b) di(ethylene glycol) 2-ethylhexyl ether, (c) tri(propylene glycol) butyl ether and (d) heptanol.

present results show that hydration of kaolinite is not necessary for the formation of halloysite-like tubes, as the reactions were carried out in organic media. Rather, the weakening of the interlayer hydrogen bonds is decisive, as proposed by Singh (1996) and proved here, by the ease of formation of kaolinite tubes when the basal spacing is expanded to more than seven times its original size. In addition, the ultrasonic treatment favoured the fast access of the organic solvent to the interlayer spaces and promoted the separation process.

Typical natural halloysite tubes have external diameters between 50 and 500 nm (Singh, 1996; Bates *et al.*, 1950). The smallest tubes have a diameter of not less than 40 nm, which corresponds to a rolled particle composed of ~14 layers. Such

tubes were obtained by the ammonium or potassium acetate treatment of kaolinite (Weiss & Russow, 1963; Singh & Mackinnon, 1996). The tubes obtained by the process described here show distinctly smaller external diameters. The smallest diameter was ~25 nm. Bates *et al.* (1950) calculated the smallest inner diameter for a rolled single kaolinite layer to be 25.08 nm. Thus the smallest tubes we prepared are probably composed of rolled single kaolinite layers or contain only a few layers, and the maximum degree of delamination of kaolinite was possibly achieved. In further experiments, the delaminated ungrafted kaolinite was again submitted to an intercalation/deintercalation process. This yielded a much higher proportion of tubes and much fewer platy particles (results not
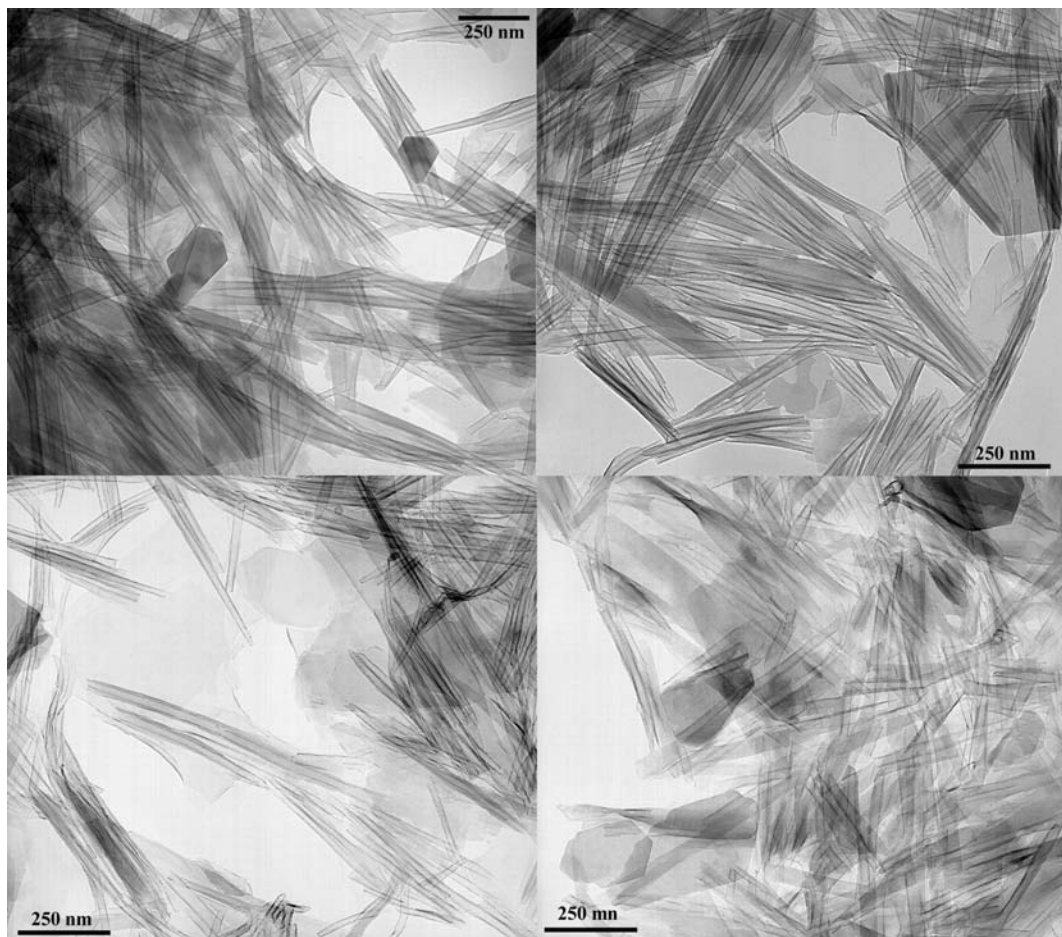
FIG. 9. TEM images of the deintercalated kaolinites grafted with 1,3-butanediol, di(ethylene glycol) 2-ethylhexyl ether, pentanol and heptanol (from left to right, from top to bottom).

shown). Thinner tubes or different morphologies were not found.

CONCLUSIONS

Grafted derivatives of kaolinite directly intercalate primary n-alkylamines, in contrast to the behaviour of raw kaolinite. Deintercalation in toluene with sonification delaminated the particles into very thin lamellae that rolled to form hollow tubes. The greatest possible degree of delamination of kaolinite was possibly achieved. The smallest tubes had external diameters compatible with the value calculated for tubes formed by rolled single kaolinite layers. Interlayer grafting of the kaolinite particles promoted considerably the delamination process.

Delamination of grafted kaolinites yields nanotubes with an external silica-like surface and an inner surface with a hydrophobic/hydrophilic character controlled by the grafted molecules. This tailoring of the tube interior might be of great importance for many applications that are currently envisaged for nanotubes such as in advanced catalysis, sensor/actuator arrays, energy storage/conversion, opto-electronic devices or fixation of bio-active molecules (Dong *et al.*, 2003).

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