



# Characterization of kaolinite-cetyltrimethylammonium chloride intercalation complex synthesized through eco-friendly kaolinite-urea pre-intercalation complex



Éva Makó<sup>a,\*</sup>, András Kovács<sup>a</sup>, Richard Katona<sup>b</sup>, Tamás Kristóf<sup>b</sup>

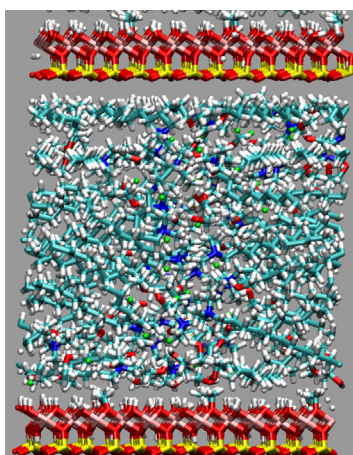
<sup>a</sup> Institute of Materials Engineering, University of Pannonia, H-8201 Veszprém, P.O. Box 158, Hungary

<sup>b</sup> Institute of Chemistry, Department of Physical Chemistry, University of Pannonia, H-8201 Veszprém, P.O. Box 158, Hungary.

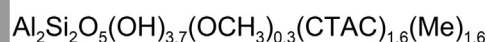
## HIGHLIGHTS

- Kaolinite-CTAC complex is produced through kaolinite-U pre-intercalation complex.
- Formation of the 3.82-nm complex causes no loss of periodicity in layer stacking.
- The formula of  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_{3.7}(\text{OCH}_3)_{0.3}(\text{CTAC})_{1.6}(\text{Me})_{1.6}$  is estimated.
- The CTAC guest molecular structure does not show any distinct layering.

## GRAPHICAL ABSTRACT



$$d_{001} = 3.82 \text{ nm}$$



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## ABSTRACT

Because of its suitability for producing kaolinite nanoscrolls, the kaolinite-cetyltrimethylammonium chloride intercalation complex is of interest in the research area of kaolinite nanocomposites. Experimental and molecular simulation analyses are used to investigate this intercalation complex, revealing its real structure formed through partially methoxy-modified kaolinite. Cost-efficient homogenization method is applied to synthesize the eco-friendly kaolinite-urea pre-intercalation complex, which was found to be favorable to intercalate cetyltrimethylammonium chloride into the interlayer space of kaolinite. The influence of the pre-intercalated urea molecules, the partial modification of kaolinite structure with methoxy groups, and the presence of methanol molecules in the interlayer space of kaolinite on the intercalation of cetyltrimethylammonium chloride is characterized experimentally by X-ray diffraction, thermal analysis, Fourier transform infrared spectroscopy, and electron microscopy. The kaolinite-cetyltrimethylammonium chloride complex is identified at the basal spacing of 3.82 nm with the chemical formula of  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_{3.7}(\text{OCH}_3)_{0.3}(\text{CTAC})_{1.6}(\text{Me})_{1.6}$ . Our molecular simulations predict methanol-containing structures between methoxy-functionalized kaolinite layers with diffuse guest molecular arrangements.

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\* Corresponding author.

E-mail addresses: [makoe@almos.vein.hu](mailto:makoe@almos.vein.hu) (É. Makó), [andree0717@gmail.com](mailto:andree0717@gmail.com)

(A. Kovács), [ricsidome@gmail.com](mailto:ricsidome@gmail.com) (R. Katona), [kristoft@almos.vein.hu](mailto:kristoft@almos.vein.hu) (T. Kristóf).

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## 1. Introduction

Various organic compounds (e.g. dimethyl sulfoxide, urea, *N*-methylformamide) can directly be intercalated into the inter-layer space of kaolinite breaking up the hydrogen bonds between the double layers [1–41]. Kaolinite-dimethyl sulfoxide (kaolinite-DMSO), kaolinite-urea (kaolinite-U), and kaolinite-*N*-methylformamide (kaolinite-NMF) pre-intercalation complexes are successfully applied to synthesize advanced exfoliated kaolinite nanocomposites [18,19,25,29–31,34,35,40]. The preparation of these nanocomposites is usually carried out through multiple intercalations, where the natural platy kaolinite could transform from nanoplates into halloysite-like nanoscrolls. A promising exfoliation method for synthesizing kaolinite nanoscrolls involves the intercalation of cetyltrimethylammonium chloride (CTAC) into a kaolinite-methanol (kaolinite-Me) complex prepared from kaolinite-DMSO or kaolinite-NMF pre-intercalate [19,29,30,34,35,40].

The frequently used precursors of the kaolinite-CTAC/kaolinite-Me complex (DMSO and NMF) are toxic and their industrial applications should be minimized [7,19,20,29,30,33–36,38,40], while U is a non-toxic reagent and can intercalate into kaolinite in one step. To our knowledge, the preparation of kaolinite-CTAC complex using U as precursor was not published before. Direct intercalation of U into kaolinite was carried out using solution [1,2,4,8,9,16,20,26,28,34,37,38], mechanochemical (co-grinding) [13,21–23,25–28,31,32,37], and homogenization [41] techniques. These techniques resulted in high degree of intercalation, but the mechanochemical and homogenization techniques require less time and consume an order of magnitude less chemicals. According to our recent studies, higher degree of intercalation was obtained by the homogenization method than by the solution one, and the homogenization treatment (contrary to the mechanochemical one) does not reduce the amount of the crystalline kaolinite phase and does not crack the kaolinite layers (this latter may cause difficulties in the formation of kaolinite nanoscrolls). Lately, we [41] applied the one-step homogenization technique to intercalate U.

Various researches [7,10,12,15,19,20,29,30,33–36,38,41] proved that kaolinite-DMSO and kaolinite-NMF complexes are effective pre-intercalates to form kaolinite-Me complexes. From the DMSO and NMF pre-intercalates, the formation of a kaolinite-Me complex with basal spacing of 1.11–1.13 nm was established in methanol-wet state [10,12,15,19,29,30,33–36,41], but on air-drying, a contraction down to 0.93–0.86 nm was observed [12,15,19,38,41]. Using elemental and thermal analysis results, Tunney and Detellier [7], Komori et al. [15], and Matusik and Klapayta [36] calculated the values of  $x=0.87$ ,  $x=0.36$ , and  $x=0.48$ , respectively, for the supposed chemical formula of  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_{4-x}(\text{OCH}_3)_x$  for the obtained methoxylated kaolinite structure.

In spite of the more eco-friendly behavior of U, there are only two studies reported in the literature [34,41], where the kaolinite-U pre-intercalate was used to synthesize kaolinite-Me complexes. In our previous work with U [41], we obtained the same methanol-wet state (with the basal spacing of 1.12 nm) as prepared earlier in the literature using the kaolinite-DMSO and kaolinite-NMF pre-intercalates [10,12,15,19,29,30,33–36]. However, the drying of our methanol-wet complex led to a somewhat different methoxylated kaolinite structure with  $x=0.3$ , which was far below the theoretical upper limit ratio of methoxy functionalization ( $x=1$ ) of the inner surfaces.

Molecular simulation is a valuable tool to get a more complete understanding of experimental results. To our knowledge, there are no classical molecular simulation studies for kaolinite-CTAC complexes. Using atomically detailed molecular dynamics (MD) simulations, Zeng et al. [42] studied comparable systems

with sufficiently large number of intercalated alkyl chains, but with a different clay mineral (montmorillonite). Recently, Zhang et al. [43] managed to employ such methodology for the kaolinite-dodecylamine system and found the structure to be much more complicated than the idealized structure that can be obtained from stereochemical predictions.

In our previous study [41], we presented a detailed experimental and molecular simulation characterization of the possible wet and dry kaolinite-Me complexes. As a continuation of this research, in this work we synthesized, through the wet kaolinite-Me intermediate complex, the kaolinite-CTAC intercalation complex, which was further used to get kaolinite nanoscrolls. The experimental and theoretical characterizations of this complex consider the possibility of partial methoxy-functionalization of kaolinite layers and of the presence of free Me molecules in the interlayer space.

## 2. Materials and methods

### 2.1. Samples and intercalation procedure

The high-grade Zettlitz kaolin (ZK) [26,41] was used, which contains 91 wt% of kaolinite with a Hinckley index (HI) [44] of around 0.8. Analytical grade urea (U), methanol (Me), and cetyltrimethylammonium chloride (CTAC) were used as intercalating reagent from Sigma-Aldrich, Scharlab, and Alfa Aesar, respectively.

The kaolinite-U and the kaolinite-Me complexes were prepared according to our previous work [41]. We synthesized the kaolinite-U pre-intercalation complex using our homogenization intercalation procedure: simply wetting kaolin with a mixture of solid U and distilled water in an agate mortar, and aging the mixture for 19 days in closed sample holder (the aged mixture is denoted as ZK-U). The kaolinite-Me complex was made by adding the pre-intercalation sample into Me and stirring the suspension for 24 h at room temperature [41]. After that, the solid part of the sample was separated and redispersed in a fresh portion of Me, and this step was repeated 18 times. Then the centrifuged product was stored under Me for further use (the obtained kaolinite-Me complex sample is denoted as ZK-U-Me(wet)). A part of this type of sample was dried at room temperature for 24 h (it is denoted as ZK-U-Me(air-dry)).

The kaolinite-CTAC complex was prepared according to Yuan et al. [35]. 1.0 g of ZK-U-Me(wet) sample was added into 40 cm<sup>3</sup> of Me based solution of CTAC (1 M) and stirred at 80 °C for 24 h. Then the solid part was separated by centrifugation. One portion of the solid was dried (it is denoted as ZK-U-Me-CTAC(unwashed)) and the other portion was washed 6 times with fresh ethanol, to remove CTAC, and then dried at 80 °C for 24 h (the obtained sample is denoted as ZK-U-Me-CTAC(washed)).

### 2.2. X-ray diffraction (XRD) analysis

The XRD patterns were recorded using a Philips PW 3710 type powder diffractometer with CuK $\alpha$  radiation, operating at 50 kV and 40 mA, a graphite diffracted-beam monochromator, and a continuous scanning speed of 0.02°/s. Data collections and evaluations were carried out with X'Pert Data Collector and X'Pert High Score Plus software. Profile fitting option of this software was applied to determine the full width at half-maximum (FWHM) value and the integral intensity of an individual diffraction peak. According to Wiewiora and Brindley [45], the integrated peak intensities of (001) reflections was used to determine the degree of intercalation. During the XRD measurement, wet samples were covered with a polyethylene foil to avoid drying. The (002) reflection of muscovite identified by 00-058-2035 reference pattern was used for internal low-2theta calibration [46].

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