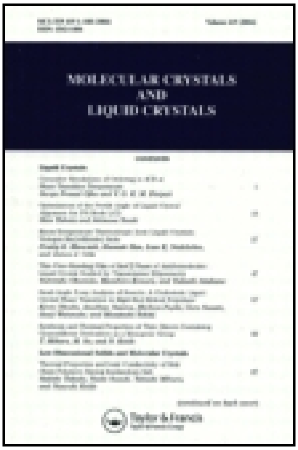

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The Chemistry of Organofunctionalized Silicon Cubanes in Swelling Smectites

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The Chemistry of Organofunctionalized Silicon Cubanes in Swelling Smectites

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Abstract: The intercalation of a cubical octamer derived from the controlled hydrolysis of 3-aminopropyltriethoxysilane with smectite clays has been examined. The organosilicon cubanes are adsorbed in an amount that exceeds the cation exchange capacity of the mineral. The excess quantity is incorporated in the form of physically adsorbed ion pairs. The results suggest that the physically adsorbed ion-paired cubic units, participate in alkylation reactions affording the corresponding tetraalkylammonium derivatives under triphase conditions. The alkylated products were studied by chemical analysis, X-ray diffraction and FT-infrared spectroscopy.

Keywords: triphase reactions, smectite, intercalation, organosilicon oligomers.

INTRODUCTION

Under controlled conditions of hydrolysis organofunctional alkosilanes of the type $(RO)_3Si(CH_2)_nA$ yield oligomeric polyhedral organosilicon derivatives which have been proved to be ideal precursors for pillaring smectite clays with silica [1]. The general formula of the oligomeric derivatives is $(ZSiO_{1.5})n$, n>4, where Z= 2-ethylpyridine, 3-aminopropyl. The aminofunctionalized derivatives can not be isolated but gel permeation chromatographic [2] and ^{29}Si NMR spectroscopic [3] studies have shown that octameric species, n=4, are predominantly formed in methanolic solution of the monomers upon addition of water. The cubane structure has been established from a single crystal X-ray analysis of the $(3\text{-}IC_3H_6)_8(Si_8O_{12})$ member [4].

In the present work we report the intercalation of a cubical octamer, denoted herein as Si_8-APTEOS,derived from the hydrolysis of the commercially available 3-aminopropyltriethoxysilane and some alkylation reactions occurring in the interlayer zone of the clays.

EXPERIMENTAL

Naturally-occuring sodium montmorillonite obtained from the source SWy-1, Crook Country Wyoming USA and the organosilane 3-aminopropyl triethoxysilane, (APTEOS), $H_2N(CH_2)_3Si(OCH_2CH_3)_3$, from Janssen Chimica, Belgium were used in this study. The APTEOS-clay complexes were prepared by reacting a 0.5% wt clay suspension with aliquots of 0.45M APTEOS solution such that the ratio, R=[APTEOS]/[clay], was 3. The n-alkyl iodides (R=methyl, ethyl) reacted with clay APTEOS complex (solid phase) under triphase conditions using toluene (organic phase) and aqueous Na_2CO_3 solution (aqueous phase) in order to prepare the alkylated products.

RESULTS AND DISCUSSION

In order to examine in detail the uptake of the Si_8-APTEOS cubes by the mineral surfaces we have determine the corresponding adsorption curve shown in Figure 1. The steep rise of the curve at low APTEOS concentrations indicates the high preference of the clay for the hydrolyzed APTEOS cations. From the plateau of the curve we observe that the amount of the adsorbed APTEOS corresponds to 1.8 times the cation exchange capacity of the clay.

The excess uptake of APTEOS can be attributed to the formation in the interlayer zone of the clay of ion-paired units such as $[H_3N(CH_2)_3Si_8O_{12}][X^-]_8$. In previous studies such ion-pair formation has been proposed for the binding of tris-bipyridyl or tris-phenanthroline metal chelates to the surfaces of smectite clays [5].

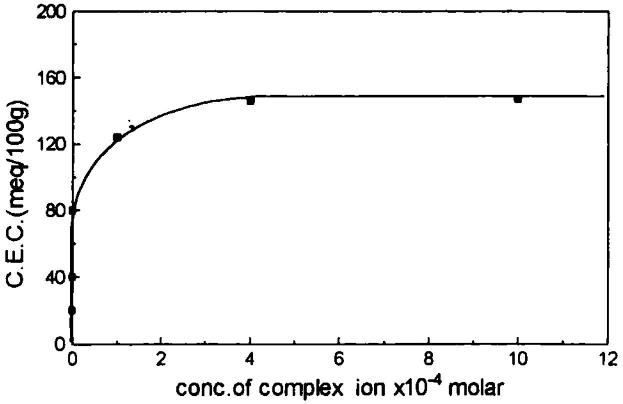

FIGURE 1. Adsorption isotherm of Si_8-APTEOS cubes on Na-montmorillonite.

The XRD patterns of the Na^+-saturated montmorillonite and of the product obtained after the intercalation process and triphase reactions are shown in Figure 2.The spectrum of the Na^+-clay sample (a) exhibits a single peak at 12.7Å which corresponds to an interlayer distance of 3.2Å, characteristic of the expansion of the clay by the presence of hydrated sodium cations. When the clay was treated with APTEOS solution the XRD peak for an unwashed product (b) shifted to 19.1Å, indicating of the intercalation of the cubic species into the clay interlayers. Repeated washings of the sample caused a significant lowering of the d-spacing from 19.1Å to a value of 16.5Å. This decrease is attributed to the removal of ion-pairs units from the clay interlayer. After the alkylation reactions the XRD peak was shifted from

19.1Å to 20.6Å as shown in figure 2(b-d). This shift, which corresponds to a gradual increase in the interlayer distance from 0.8Å to 1.5Å can be attributed

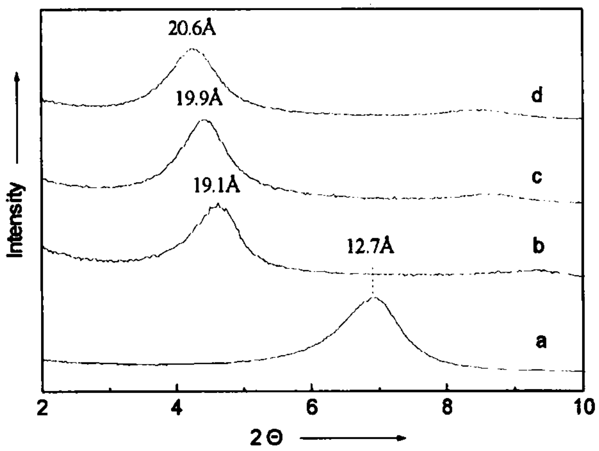

FIGURE 2 XRD pattern of the original clay (a), after intercalation with Si_8-APTEOS cubes (b) and after triphase reactions: methylation (c), ethylation (d).

to the substitution of the hydrogen atoms of RNH_3^+ groups by the larger in size alkyl groups such as $-CH_3$ and $-C_2H_5$. Two observations are of particular merit. At first, the alkylation reactions do not occur after a thoroughly washing of the clay which removes the physically adsorbed ions-pairs units. In addition, in polar solvents, such as alcohol's or water, the NH_2 group on the third carbon atom from silicon has been found to be virtually inert [6]. A schematically illustration of the alkylation reactions is shown in Figure 3.

Figure 4 shows the infrared spectra in the frequency region 1350-1600 cm^{-1} of the original clay and the clay-organosilicon cubanes products. The spectrum of the intercalated clay with Si_8-APTEOS cubes exhibits the strongest bands at 1560cm^{-1} and 1500cm^{-1}. These bands are assigned to the asymmetric deformation of NH_3^+ groups [7,8]. Specifically the band at

$1500 cm^{-1}$ originates from a vibration in which the C_3 axis of NH_3^+ group is parallel to the layers, while the band at higher frequency ($1570 cm^{-1}$) is due to

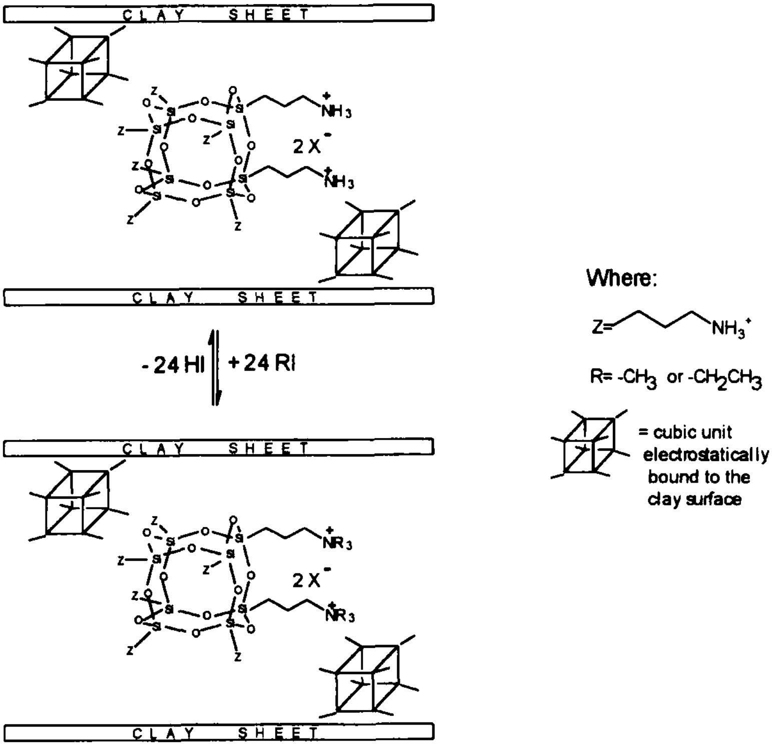

FIGURE 3 The triphase reactions into the clay interlayer

a similar vibration however with the C_3 axis in its normal position to the layers [8]. In addition, the large upshift in frequency suggests hydrogen-bonding interactions between the NH_3^+ groups and the surface oxygens. The weak bands at lower frequencies are attributed to the bending vibrations of CH_2 and CH_3 groups. The alkylation of the Si_8-APTEOS cubes change drastically the spectrum as shown in Figure 4(c-d). The new bands appearing at $1490 cm^{-1}$ and around $1475 cm^{-1}$ arise from the asymmetric N^+-CH_3 deformations, while the weaker at 1420cm^{-1} can be attributed to a scissoring vibration of methylene groups adjacent to charged nitrogen of the Si_8-APTEOS cubes.

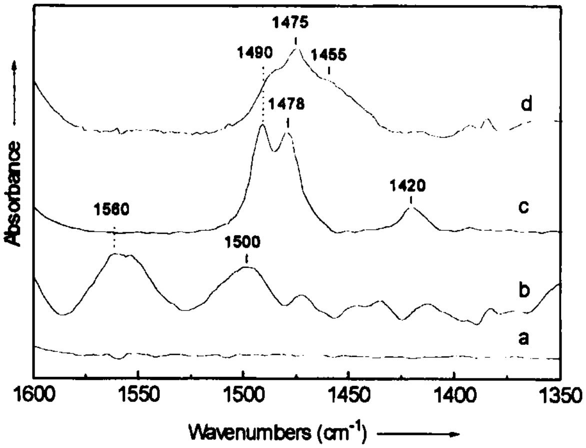

FIGURE 4 Infrared spectra of the original clay (a), after intercalation with Si_8-APTEOS cubes (b) and after triphase reactions: methylation (c), ethylation (d).

The broad band at 1455cm^{-1} in the spectrum of ethylene product (d) can be attributed to the CH_2 vibrations of aliphatic chains [9], indicating the alkylation of Si_8-APTEOS cubes.

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