DECOMPOSITION OF ALKYLAMMONIUM CATIONS INTERCALATED IN VERMICULITE

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The phenomenon of alkylammonium decomposition on montmorillonite surfaces has been studied by several researchers. In 1964, Calvet et al. showed that it was possible to transform alkylammonium cations adsorbed on montmorillonite surface at temperatures considerably below the theoretical decomposition temperatures of amines or their chlorhydrates. Above 100ºC, in presence of oxygen, the cations decompose into \( \text{NH}_4^+ \) (which remains on the clay), organic residues and hydrocarbons. The observations were interpreted as the result of catalytic break of the C-N bond. The catalytic effect was attributed to protons of the water adsorbed on the montmorillonite surface.

Durand et al. (1972) have studied in an inert atmosphere the thermal transformation of alkylammonium cations adsorbed on the surface of a montmorillonite in various conditions of hydration. The reactions observed were mainly transalkylations, for which a mechanism of acid catalysis was proposed. A high degree of dissociation of the water remaining on the surface of the clay was required for these processes.

There are some differences between the thermal transformation of alkylammonium montmorillonite in an inert atmosphere and the corresponding transformation in presence of oxygen. In the latter, a faster increase of the \( \text{NH}_4^+ \) content was observed, and transalkylation processes do not operate.

The aim of this paper is to determine the decomposition of decylammonium cations on vermiculite surface, as a result of the acidity of the medium.

The vermiculite used was obtained from the "Santa Olalla" deposit in Huelva, Spain, and it was saturated in decylammonium cations, according to the method proposed by Lagaly and Weiss (1969).
The decylammonium-vermiculite complex was treated with solutions of HCl in water and butanol, and solutions of N'- (4-chloro-2-methylphenyl)-N,N-dimethyl methanoimidamide hydrochloride in butanol, which produces an acidity similar to the HCl solutions.

The treatments were carried out at 60°C in stoppered glass tubes. The solutions were changed weekly up to 100 days of treatment; from that time on, the solutions were left in contact with the samples without further change until a year passed.

The X-ray diffraction pattern and the infrared spectra of alkylammonium-vermiculite complex do not show changes after treatment with deionized water or butanol.

The basal spacing of decylammonium-vermiculite complex changes from 21.21 Å to 12.8 Å after several treatments with HCl solution in water or butanol. The latter diffraction increases to about 14 Å if the solutions are kept in contact with the samples without any change.

In the infrared spectrum of the sample showing a 12.8 Å diffraction, bands appear at 1430, 3240 and 3040 cm\(^{-1}\) corresponding to ammonium cations present in the interlamellar spaces (Ahlrichs et al., 1972; Stone and Wild, 1978). The ammonium is produced by the break of the C-N bond of alkylammonium due to their high degree of surface acidity present as a consequence of the pH in the solution used.

When the solution are kept unchanged, the experimental data show the release of Mg\(^{2+}\) ions from the vermiculite structure due to the acidity of the medium. This Mg\(^{2+}\) displaces the alkylammonium and ammonium from interlamellar space. The ammonium is exchanged completely in the samples treated with aqueous solution, whereas in butanol solution it is partially displaced. The 1430 cm\(^{-1}\) absorption band corresponding to NH\(^+\) is displaced to 1400 cm\(^{-1}\) due to release of structural Mg\(^{2+}\), producing a higher lamellar charge and increasing the interaction between NH\(^+\) ion and the surface.

The decomposition of decylammonium cations on the vermiculite surfaces is also produced when the decylammonium vermiculite complex is treated with a solution of an organic compound (N'- (4-chloro-2-methylphenyl)-N,N-dimethyl methanoimidamide hydrochloride) in butanol. In this case the C-N bond breaking is due to the high acidity which is produced by dissociation of the scarce water molecules remaining in the interlamellar space.
REFERENCES


