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Abstract

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Organic Derivatives of Kaolin

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The formation of a covalent bond between an organic radical and a silicate macromolecule was, until recently, called into question by a number of authors ([1,2]). Later studies, however, convincingly demonstrate, on the basis of data from differential thermal analysis ([3–5]), infrared spectroscopy ([4,6,7]), and X-ray structural analysis ([8]), the possibility of the existence of organic derivatives of silicates with a layered structure. The object of these investigations was chiefly montmorillonite—a mineral rich in surface-active hydroxyl groups, the replacement of which by organic radicals served as one of the most frequently used methods for synthesizing organic derivatives.

As for organic derivatives of kaolin, information on them is absent from the literature, with the exception of a brief report, not confirmed by experimental data, that ground kaolinite can be etherified when treated with propylene oxide ([9]). We have attempted to obtain organic derivatives of kaolin, which are of definite theoretical interest and are also of interest from the standpoint of their practical application.

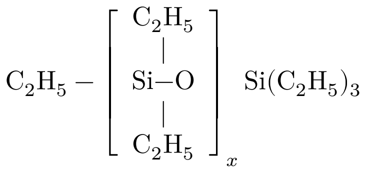
As the object of investigation we used Chinese kaolin from the Suzhou deposit, which in chemical composition is almost pure kaolinite.

Chemical composition of Chinese kaolin (in percent)

SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	K_2O+Na_2O	Active OH groups	L.o.i.	SiO_2/Al_2O_3
4.81	39.76	Traces	0.16	0.24	0.37	0.05	0.57–0.61	14.97	1.89

Electron-microscopic study of samples of the original kaolin made it possible to determine that the bulk of it consists of particles with sizes of 0.1–1.0 μ (66–68%) and 1.0–3.0 μ (30%). The choice of this mineral was due to the fact that kaolinite, as is known, has a low cation-exchange capacity, and the amount of organic cations sorbed by it is extremely small ([10]). Organic molecules do not penetrate between the elementary layers of kaolin; adsorption occurs only near the edges and on the external surface of the mineral (^{11}). Subsequently, in isolating the organic derivatives of kaolin, this greatly facilitated the work connected with the need for complete removal of adsorption products.

The organic derivatives were obtained by us by disintegrating kaolin with the aid of ultrasound in a medium of such organic compounds as diphenyl, diphenylmethane, and also in a medium of an ethylpolysiloxane liquid. A polyethylene beaker containing a mixture consisting of 3 g of kaolin and 29.5 g of polymer homologs of ethylpolysiloxane of the general formula



$$C_2H_5 - \left[\begin{array}{c} C_2H_5 \\ | \\ \mathrm{Si{-}O} \\ | \\ C_2H_5 \end{array} \right]_x \mathrm{Si}(C_2H_5)_3 \qquad (x = 8, 9),$$

was placed on a magnetostrictive vibrator operating in the frequency range 20–20.6 kHz. The beaker and the vibrator were cooled in a bath with running water. Grinding was carried out in three 10-min stages, each with intervals for cooling the reaction mass. The use of ultrasonic vibrations for the mechanochemical synthesis of organic derivatives of kaolin made it possible for us to carry out effective grinding without deformation of the crystalline structure of the aluminosilicate and under mild temperature conditions (not above 90°).

After grinding was completed, the mixture was washed with benzene to remove ethylpolysiloxane that had not entered into the reaction. The completeness of washing was monitored by spectral analysis of the wash portions of benzene for silicon content. The product treated in this way was dried in air at 150–170° for 7 h. Complete removal of benzene was established by the absence in the infrared spectrum of frequencies corresponding to the valence vibrations of the benzene molecule. The product obtained contained 0.2% carbon.

Ethylpolysiloxykaolin was a white powder which, when wetted with benzene, acquired a brown color. The powder possessed a high degree of hydrophobicity ($W = 17$ erg/cm^2).

In the same way, from a mixture of 6 g of kaolin and 29 g of diphenyl, the phenyl derivative of kaolin was obtained, and from a mixture of 12 g of kaolin and 58 g of diphenylmethane—the phenylmethyl derivative. The first of these derivatives had a blue color which, when the powder was wetted with benzene, changed to an intense dark blue; the second had a gray color, becoming dark green when the powder was wetted with benzene. The carbon content in the phenyl derivative was 0.1%, and in the phenylmethyl derivative 0.3%.

The mechanism of formation of such organic derivatives may be represented as follows. Ultrasonic vibrations cause the appearance of organic radicals, as well as active particles, due to rupture of the siloxane and alumosiloxane bonds in kaolin.

The active particles that appear recombine, forming an organic derivative of the aluminosilicate:

$$\begin{matrix}\equiv \mathrm{Si}\\ \equiv \mathrm{Si}\end{matrix}\!> \mathrm{O} + \mathrm{R}-\mathrm{R}' \rightarrow \left[\begin{matrix}\equiv \mathrm{Si}^{(+)} & -\mathrm{R}\\ \equiv \mathrm{Si}-\mathrm{O}^{(-)} & -\mathrm{R}'\end{matrix}\right] \rightarrow \begin{matrix}\equiv \mathrm{Si}-\mathrm{R}\\ \equiv \mathrm{Si}-\mathrm{O}-\mathrm{R}'\end{matrix},$$

where R, R′ are organic radicals.

Obviously, the formation of an organic derivative, preceded by rupture of the alumosiloxane bond, can be represented in the same way:

$$\begin{matrix}\equiv \mathrm{Si}\\ \equiv \mathrm{Al}\end{matrix}\!> \mathrm{O} + \mathrm{R}-\mathrm{R}' \rightarrow \left[\begin{matrix}\equiv \mathrm{Si}^{(+)} & -\mathrm{R}\\ \equiv \mathrm{Al}-\mathrm{O}^{(-)} & -\mathrm{R}'\end{matrix}\right] \rightarrow \begin{matrix}\equiv \mathrm{Si}-\mathrm{R}\\ \equiv \mathrm{Al}-\mathrm{O}-\mathrm{R}'\end{matrix}.$$

It should be taken into account that rupture of the alumosiloxane bond is less probable, since splitting of kaolin particles under the action of ultrasonic vibrations occurs more readily in the direction perpendicular to the cleavage plane.

If organic compounds are used as the medium, derivatives with Si-C and Si-O-C bonds are formed; in the case of grinding in a polysiloxane medium, new bonds of only one type are formed, Si-O-Si $(\mathrm{R})_2$.

As X-ray structural analysis showed, modification of the kaolin samples did not lead to a change in the interplanar spacings. This indicates that the organic groups are fixed only on the surface of the mineral. The obtained samples of organic derivatives of kaolin were subjected to differential thermal analysis (Fig. 1). Since, upon loss by kaolin of hydroxyl groups in the range 520-670° (Fig. 1, *I*), a considerable endothermic effect is manifested, and in this same range one could expect the appearance of an exothermic

effect caused by combustion of the organic part of the derivatives, it became necessary to compensate for the effect of the endothermic reaction. Such compensation was achieved when the original kaolin was used as the reference sample. This made it possible to detect the exothermic effect of combustion of the organic constituent for the organic derivatives obtained. For the diphenyl derivative, the maximum of the exothermic effect appeared at a temperature of 580° (Fig. 1, *III*), for the diphenylmethyl derivative at 505° (Fig. 1, *IV*), and for the ethylpolysiloxy derivative at 620° (Fig. 1, *VI*). The exothermic effect of combustion of the organic part of the diphenylmethyl derivative, which did not fall within the region of the endothermic effect associated with loss of the crystal lattice of hydroxyl groups, could also be observed on a differential curve recorded by the usual method, i.e., when aluminum oxide was used as the reference sample (Fig. 1, *V*).

Fig. 1. Curves of differential thermal analysis of kaolin and its organic derivatives. *I* —original kaolin; reference —aluminum oxide; *II* —original kaolin; reference —original kaolin; *III* —diphenyl derivative of kaolin; reference —original

Fig. 1. Differential thermal analysis curves of kaolin and its organic derivatives.

Figure 1: Fig. 1. Differential thermal analysis curves of kaolin and its organic derivatives.

kaolin; *IV* –the same; reference –original kaolin; *V* –the same; reference –aluminum oxide; *VI* –ethylpolysiloxane derivative of kaolin; reference –original kaolin; *VII* –kaolin heated at 90° for 6 hr with ethylpolysiloxane liquid, followed by treatment with benzene and drying; reference –original kaolin; *VIII* –kaolin with adsorbed ethylpolysiloxane liquid; reference –original kaolin.

The difference in the behavior of covalently bonded organic groups and molecules held on the surface of kaolin by adsorption forces is clearly seen when comparing differential curve *VI*, obtained in the study of the ethylpolysiloxane derivative of kaolin, with curve *VIII*, which characterizes the combustion of ethylpolysiloxane adsorbed on kaolin.

Prolonged heating (90°) of the initial mixture of kaolin and ethylpolysiloxane without ultrasonic grinding does not lead to the formation of an organic derivative of kaolin. After thorough washing with benzene and subsequent drying, the sample was subjected to differential thermal analysis (curve *VII*). Curve *VII* shows considerable similarity to the differential curve of the initial kaolin (curve *II*) and the absence of an exothermic effect in the region 570–650°, characteristic of the ethylpolysiloxane derivative of kaolin (curve *VI*).

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Note: Figure translations are in progress. See original paper for figures.