Clay Minerals: Adsorbophysical Properties

O Kotova
Science secretary, Institute of Geology KomiSC UB RAS, Syktyvkar, Russia
Email: kotova@geo.komisc.ru

Abstract. The structure and features of surfaces of clay minerals (kaolin, montmorillonite, etc) have an important scientific and practical value. On the surface the interrelation of processes at electronic, atomic and molecular levels is realized. Availability of mineral surface to external influences opens wide scientific and technical opportunities of use of the surface phenomena, so the research of crystal-chemical and crystal-physical processes in near-surface area of clay minerals is important.

After long term researches of gas-clay mineral system in physical fields the author has obtained experimental and theoretical material contributing to the creation of the surface theory of clays. A part of the researches is dedicated to studying the mechanism of crystal-chemical and crystal-physical processes in near surface area of clay mineral systems, selectivity of the surface centers to interact with gas phase molecules and adsorbophysical properties.

The study of physical and chemical properties of fine clay minerals and their modification has a decisive importance for development of theory and practice of nanotechnologies: they are sorbents, membranes, ceramics and other materials with required electronic features.

1. Introduction
The surface of clay minerals is a nice experimental site to study mechanisms of natural processes. Interaction of mineral surfaces and the gas simple molecules plays important role in a wide range of investigations: from the synthesis of prebiotic organic molecules to modern reactions of weathering, from metal implants in human body to concentrating processes, from the life origin to survival problems. In any case we will speak about finding of such relations as rates of reactions and transformations on the physical parameters and mechanisms, which are laid into basis of models allowing to determine and predict natural processes, to create new technologies. Clays are fine particles, where surfaces can be considered as a special state with own physics and chemistry. Knowledge of the nature of clay became better understood in the 1930s with advancements in x-ray diffraction technology necessary to analyze the molecular nature of clay particles. By their properties and reactivity surfaces at some extent are similar to crystal volume and gas molecule, but due to differences they are related to special field of activity.

Among numerous methods of investigation of the surface and subsurface of particles, of particular interest is the method proposed by the Russian scientist A.Terenin [1] in the middle of the 20th century. The method is based on the study of the photoinduced processes from the interaction of the molecules of the gas phase with the surface of the material. The method is based on the various bonds existing between the molecular and electronic processes in the adsorbed layer, and in the subsurface area of materials. Teredin and his followers in Russia tried to update the zone theory by incorporation of the achievements in the chemistry of surfaces, in the areas of adsorption and catalysis. Other scientists also made similar attempts. Roald Hoffmann published the results of some such studies in...
his well-known treatise "Solid and Surfaces: A Chemist’s View of Bonding in Extended Structures" [2]. The author now uses this experience in applied mineralogy problems of clay.

2. Materials
A number of clay minerals have been studied (kaolin, montmorillonite, quartz, rutile, ilmenite, hematite, etc.). Clay minerals are usually ultrafine-grained (less than 2 micrometres).

Major chemical components of the clays are SiO$_2$ (30-70%), Al$_2$O$_3$ (10-40%) and H$_2$O (5-10%). Smaller quantities of TiO$_2$, Fe$_2$O$_3$, FeO, MnO, MgO, CaO, K$_2$O, Na$_2$O are found. Hence the clay minerals are predominated by oxide minerals, they are good model objects to study processes in the gas-clay system. Among the studied minerals, those characterized by dense packing of the atoms (the molecules) and by large energy bonds (gold, platinum) can be initially identified. In this paper, the main adsorbophysical characteristics of precious metals are compared with clay minerals, and the basis of the adsorbophysical separating methods are discussed.

3. Methods
Clay minerals require special analytical techniques for their study. These include x-ray diffraction, electron diffraction methods, various spectroscopic methods such as Mössbauer spectroscopy, infrared spectroscopy, SEM-EDS etc.

At present there are three classes of experimental methods of investigation of surfaces. Electrical and optical measurements used at investigations of clays as semiconductors are the first class. These measurements allow obtaining more detailed information about surface local levels located near Fermi level of solid body. The second class includes spectroscopical methods, when the surface is struck by irradiation particles and (or) emits them. Investigations of those particles or formed photons inform on the surface states in a wide range of energies. The third class called chemical methods. But factually they are physical methods. Chemical methods are basic source of information about surface states of clays with dielectrical properties and also partly with semiconductor properties. Such methods include IR-spectroscope, mass-spectrometry, thermodesorption methods and some others.

4. Gas-clay system
The problems associated with the gas-clay system are best illustrated by the study of oxide minerals.

In general, the composition of these minerals can be given as [Me$^{n+}$O$^{2-}$] (henceforth: MeO). The chemical bond in these materials is mainly ionic in character, in some crystals with a considerable degree of covalence.

The subsurface area of clay minerals can be studied by the photoinduced processes taking place on the active surface centres. The following stages in these processes should be studied: absorption of light, migration of excitation energy, defect-formation, etc. Stage (1) is important in understanding the photoinduced processes:

$$\text{MeO} + \text{hv} \rightarrow e^- + e^+ \quad (1)$$

Low-coordinated ions of oxygen occurring at a charge state close to (-1) participate in dark processes on the mineral surface. Such ions possess similar properties to the photoinduced hole centres. A characteristic of the dark version of the process is the absence of stage (1) and, consequently, it is less amenable to the gradual ("step-by-step") research of the processes.

A characteristic of several of the systems studied, despite specific features appearing on excitation in different spectral areas, is the formation of paired centres consisting of an electron and a hole (see (1)). In the case of irradiation of fine particles outside their own region of adsorption, hole centres of the type O$^-$ appear:

$$(\text{MeO})_S + \text{hv} \rightarrow e^- + e^+ \rightarrow \text{O}^- + e^- \quad (2)$$

Mass-spectrometric and manometric studies of the surface mineral centres, carried out by the author and several other scientists have demonstrated that the electrons and holes located on the surface defects act as the photoadsorption centres for both acceptor and donor gases. These centres
have been studied by EPR method. Due to the ability of the surface centres to react selectively with the molecules of the gas phase, there appears to be an opportunity not only to separate the surface centres from the volumetric centres, but also to create deficiencies in the electronic (or hole) centres. Such method to change electronic properties of a surface of clays is very important for competitive materials and technology processes.

5. **Structure of the hydroxyl cover**
The surface of crystal particles of clay minerals usually is covered with OH-groups, which are characterized by a number of bonds of hydroxyl oxygen with an atom of metal (or non-metal) of the crystal. The number of atoms of the metal (or non-metal), surrounding oxygen of OH-groups, will always be less than the coordination number of oxygen in the lattice of oxide crystal.

\[
\text{H} \\
\text{O} \quad \text{H} \\
\text{Me} - \text{O} - + \text{H}_2\text{O} \rightarrow - \text{Me} - \text{O} -
\]

\[(3)\]

The most complete information on hydroxyl cover is given by IR-spectroscopy of adsorbed molecules. A.A. Tsyganenko [3] and a number of other authors distinguish OH-groups, which atom of oxygen is connected with one, two, three and other atoms of metal, naming them for brevity OH-groups of type I, II, III, etc.:

“Bridge” OH-groups should be thermally more stable. It is considered that “bridge” groups are corresponded to by a higher frequency of OH bond fluctuation.

In clay minerals (silica and aluminum) ions Si and Al have tetrahedral coordination relating to oxygen or hydroxyl.

6. **Influence of molecular processes on the electronic properties of clay**
The chemical and physical properties are determined under structure of hydroxyl cover of clay minerals. OH-groups on the surface of mineral particles possess negative charge, i.e.

\[Q_S^- = \sum_{i=1}^{n} q_{S_i}^-\]

where \(q_{S_i}^-\) - charge on the surface of i particle.

Presence of charge with sign "minus" results in occurrence of an opposite charge ("hole") in near-surface area. At dehydration of surfaces "holes" can emerge on the surface, forming positive not compensated charge \(Q_S^+\) on the surface.

Quartz, corundum, rutile, ilmenite, hematite and other minerals were subject to dehydration, on which surface the formation of surface non-compensated charge \(Q_S^-\) was observed, which value depended on the degree of dehydration (Fig. 1), their nature and the sizes (Fig. 2).

So, for example, \(Q_S^+\) for quartz is 2 times less, than \(Q_S^+\) for rutile with other conditions being equal. Minerals, under similar conditions with \(Q_S = 0\), were determined. It is, for example, gold, platinum and diamond - single-element minerals with dense packing and a high bond energy between atoms (ions) [4].

Molecules of gas phase of acceptor nature (oxygen, carbon dioxide) interact with electronic centers, forming various adsorption forms. According to thermodesorption spectra received after heating of rutile, the adsorbed molecules of oxygen and carbon dioxide possess \(E_a = 150\) kJ/moll.
("leave" the surface at $T \sim 673$ K). At heating quartz and monazite to 637 K a negative charge $Q_S$ occurs on the surface, which can be formed at desorption of acceptor gases.

**Figure 1.** Dependence of $Q_S$ on the degree of surface dehydroxylation (on heating temperature) of the sample (Qualitatively analogous curves have been received for all studied samples)

Thus, due to adsorption processes it is possible to receive on the surface of particles of minerals $Q_S > 0$, $Q_S < 0$ and $Q_S = 0$.

7. Adsorboelectrostatical properties

The current work has demonstrated that the increase of $Q_S$ value varies directly with the decrease in the particle size, and when the particles size is less than 0.3 mm reaches the same order as $Q_V$. Therefore, if there exists in the gas–clay system conditions for formation of the noncompensated surface charge $Q_S$, it should be considered as a surface characteristic that determines the total charge of the fine clay system: $Q = Q_V + Q_S$

Destruction of the adsorption–desorption equilibrium is an essential condition for formation of the noncompensated surface charge $Q_s$. The imbalance of adsorption–desorption equilibrium is a result of adsorption, photosorption and desorption of the donor (acceptor) molecules of the gas phase.
Usually, charging of a particle is influenced by the electrical properties of the material, e.g. the conductivity. Gold, galena, rutile, ilmenite and grains of some other minerals possessing similar conductivity may occur in the conductive fraction, and in the nonconductive fraction, diamond, corundum, quartz.

From the data above it is evident that when formation of the noncompensated surface charge \( Q_S^+ \) occurs, it is possible to separate conductive and nonconductive particles based on their surface properties. The fine particles of gold and diamond have similar adsorption properties. If the mechanism of an inductive charging is suppressed, the fine particles will be charged only by adsorption [5].

8. Adsorbomagnetical properties
As the surrounding atoms on the surface differ from those in the volume, it can be assumed that the magnetic properties of a crystal surface will also essentially differ from those in the volume. Our studies have shown that the magnetic properties of magnetite, ilmenite and hematite inside the particles differ from the magnetic properties on their surfaces and these magnetic properties have a complex interrelation. Moreover by increasing the number of adsorbed molecules of the gas phase (not depending upon the character of the adsorbate) there is a tendency for reduction of the \( M \) value (where \( M \) is magnetic permeability): \( M = M_V + M_S \)

The state of the surface has a practical influence only to the magnetization of particles at the surface [6].

9. Adsorboluminescence properties
The phenomenon of photoinduced adsorboluminescence was discovered by Andreev and Kotelnikov in the \( \text{H}_2-\text{Al}_2\text{O}_3 \) system, and later in several other systems [7], including studies by Kotova [4], of \( \text{ZrO}_2, \text{TiO}_2, \text{MgO} \) etc. The phenomenon of photoinduced adsorboluminescence is luminescence appearing as a result of chemosorption of hydrogen-containing molecules on the synthetic oxides – analogues of clay minerals. These oxides have previously been irradiated in a vacuum with waves of length 190–130 nm [7] or with a mercury lamp (according to the author’s data). The phenomenon of photoinduced adsorboluminescence allows characterization of the energetic side of the process of dissociative photosorption.

The process of dissociative adsorption of molecules of the \( \text{HR}^+ \) type (\( \text{CH}_4, \text{C}_2\text{H}_4, \text{C}_2\text{H}_6 \)) on the photoinduced hole centres is accompanied by a substantial amount of adsorption energy. Photoinduced adsorboluminescence provides information on the energy of processes occurring at the surfaces of fine clay mineral. As this phenomenon has a high probability of occurrence in clay minerals and (due to some specific features of its mechanism) zero probability of occurrence on gold, platinum and diamonds, it can be used as the basis of adsorboluminescence methods of mineral separation.

10. Optical properties
Adsorbophysical fields influence specifically the optical properties of fine clay minerals. It has been shown that the defect formation in crystals, caused by the breakdown of low-energy excitations, is characteristic of the wide-zone fine clay minerals but also occurs in the halogenides of some alkali metals. Kotova [4] and others [8] have observed formation of defects in regular and defective regions of the surface in several fine mineral systems. It has been shown that the hydroxyl cover of the surface plays an important role in the process of colour changes in the fine mineral sands. This has been proved by experiments on samples of quartz sands from weathered crusts (Subpolar Urals). A characteristic of these samples is the typical large specific surface, due to the occurrence of superfine particles, “stuck” on the surfaces of particles of average size in the fine particle system [5].

Adsorbophysical fields influence optical parameters of fine mineral systems. It is revealed that wide band fine mineral systems are not characterized by defect formation in volume of crystal in regular lattice due to disintegration of low-energy excitation, as it occurs on halogenides of alkaline metals. At the same time these processes take place on the surface of even these crystals. The defect
formation in regular and actual defective areas of surface was observed on a number of fine oxide systems. It is shown that a greater role in change of color of fine oxide mineral systems is played by surface hydroxyl cover. It is proved by experiments on the change of color of fine quartz sand of weathering crusts (Subpolar Urals Mountains) characterized by a large specific surface due to the presence of superthin particles, “sealed” on particles of basic fine environment.

Similar results were obtained by Ryabchuk [8], who revealed the centers of color of two types with maxima of absorption bands 850 and 450 nm that leads to intensive coloring of sample in dark blue and yellow colors as a result of photosorption of hydrogen and oxygen accordingly.

As a conclusion it is possible to mention that influence of adsorbophysical fields in fine clay minerals is caused by:

1) close relations between molecular and electronic processes, proceeding in these systems;
2) adsorbophysical fields become expressed (i.e. become comparable, say, with electric ones) at rather small sizes of crystals, for which \( V/S \leq L \), where 
\( S \) - area of surface; 
\( V \) - volume of crystals; 
\( L \) - length of shielding (usually \( L \approx 10^{-3} - 10^{-5} \) cm) [4].

**11. Conclusions**

To study clay surface a model is suggested, where by means of surface reactions the connection between molecular processes in adsorbed phase and electron processes in near-surface are of mineral is determined. Adsorbed molecules change surface electron states, create new, the latter affect physical and chemical characteristics of fine clay minerals resulting in new features (e.g. adsorbophysical).

One of the ways of identification of surface centers of clay minerals is their selectability to interaction with gas phase molecules of acceptor or donor nature. Blocking of surface centers in physical fields by simple molecules of gas phase of a certain nature results in changes of surface centers of fine clay minerals. Photoactivated forms of surface structural oxygen of clay minerals can be active surface centers.

Clay minerals represent a part of natural system, which can perform functions of regulating of atmosphere composition and natural processes. Mechanisms of these processes are the basis of ecologically safe technologies.

This work is supported by Projects 12-T-5-1022 and 12-5-6-016-ARCTIKA under UB RAS Program.

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