INVESTIGATION OF THE INTERACTION OF PYRIDINE WITH THE SURFACE OF LAMINAR SILICATES BY THE METHOD OF OPTICAL ELECTRONIC SPECTROSCOPY

E. G. Sivalov and Yu. I. Tarasevich

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In research practice pyridine is widely used as a convenient spectral probe for acid centers of oxide catalysts and sorbents. A study of the IR spectra of this base, sorbed on laminar silicates, has yielded a number of interesting data on the role of exchange cations and residual water molecules in the formation of their acidity [1]. However, there is no information in the literature on the use of optical electronic spectroscopy to study the interaction of pyridine with these sorbents, although it was noted in [2-5] that samples of mont-morillonite with K⁺, Na⁺, Li⁺, Ca²⁺, and Mg²⁺ cations acquired a blue color as a result of the sorption of pyridine.

Pyridine itself is colorless. In the ultraviolet portion of the spectrum it has an absorption band 260 and a shoulder 270 nm, which belong to the $\pi\pi^*$ and $p\pi^*$ transitions of electrons [6]. The cation radical of pyridine, the formation of which was registered when this base was sorbed on silica gel modified with silver, thallium, lead, and cadmium chlorides [7], is characterized by an absorption band 410-420 nm.

Thus, it can be asserted that the appearance of a blue color in the sorption of pyridine by natural silicates is associated with its conversion on the surface to more complex formations, characterized by a rather developed system of conjugated π -bonds.

To expand our concepts of the nature of the active sites on the surface of laminar silicates and to identify those of them that are responsible for the indicated conversions of sorbed pyridine, the present work was undertaken.

The objects of investigation selected were Li-, Na-, K-, Mg-, Ca-, and Sr-forms of Pyzhevsk and Oglanly montmorillonites, Glukhovetsk kaolinite, and synthetic fluorohectorite. The physicochemical characteristics of the sorbents were cited in [1, 8]. The samples were preliminarily vacuum treated at 150-200° and a residual pressure of 10⁻³ torr. The cp grade pyridine was redistilled over calcined BaO, and for the final drying, it was treated with CaA zeolite, preliminarily heated at 350°C. Before the spectral measurements, pyridine in the frozen state was carefully degasified. Laminar silicates were dehydrated by thermovacuum treatment at 200°C, placed in special glass cuvettes, saturated with pyridine vapors at room temperature, and sealed. The diffuse reflection spectra were recorded on an SF-10 spectrophotometer. The corresponding uncolored forms of the minerals were used as reference samples.

Laminar silicates possess two types of surfaces, which differ in nature and concentration of active sites. On the basal faces of laminar particles of the minerals under discussion, there are chiefly exchange cations — compensators of the negative charge arising as a result of nonstoichiometric isomorphous replacements $Al^{3+} \rightarrow Si^{4+}$ and Mg^{2+} , $Fe^{2+} \rightarrow Al^{3+}$ in the tetrahedral and octahedral layers of the structure, respectively. On the side faces of the particles of laminar silicates, together with exchange cation compensators of the broken bonds, there are hydroxyl groups of an acidic (Si_OH) and basic (Al-OH, Fe-OH, Mg-OH) character and coordination-unsaturated cations Al^{3+} , Fe^{3+} , Fe^{2+} , and Mg^{2+} [1].

To answer the question of whether chemical conversions of sorbed pyridine occur on the basal or side faces of the particles of laminar silicates, let us compare the results of spectral investigations of natural and synthetic minerals. The chemistry of the basal faces of the crystals of synthetic fluorohectorite is the same as in its natural analogs, in particular, montmorillonite. At the same time, the absence of aluminum and di- and trivalent iron cations in the structure of this sorbent impoverishes the chemistry of the side surfaces of its crystals. On the basis of the chemical composition of fluorohectorite, it can be assumed that it is represented by coordination unsaturated Mg^{2+} cations, by Mg-F groups, and partly by Si-OH and Mg-OH groups.

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Fig. 1. Electronic diffuse reflection spectra of pyridine sorbed on the Mg form of fluorohectorite (1), Na (2), Ca (3), and Mgforms (4) of Oglanly montmorillonite, Li (5), Na (6), Mg (7), and Ca forms (8) of Glukhovetsk kaolinite.





From Fig. 1 it is evident that the conversion products of pyridine, sorbed on cationsubstituted montmorillonite samples, are characterized by distinct absorption in the region of 420-590 nm. At the same time, there are no maxima in the visible portion of the spectrum of a sample of Mg-fluorohectorite with sorbed pyridine. Thus, a comparative analysis of the spectra of natural montmorillonite and synthetic fluorohectorite permits us to draw the unambiguous conclusion that natural laminar silicates acquire a color as a result of interaction of pyridine molecules with the active sites of the side faces of their particles.

The band observed in the spectra of natural samples with sorbed pyridine (Figs. 1 and 2) in the region of 420 nm, as has already been indicated above, belongs to the cation radical of pyridine. In [9] an important role of coordination-unsaturated Fe³⁺ cations of laminar silicates in the formation of cation radicals during the sorption of organic bases was noted. According to the data of chemical analyses [1], the oxide Fe₂O₃ is contained in all three investigated representatives of natural sorbents. Its content in Glukhovetsk kaolinite ranges from 3.3 to 0.4%, in Pyzhevsk and Oglanly montmorillonite 2.8-1.4% and 1.6-1.1%, respectively.



Fig. 3. Densitograms of 2,2'- (1) and 4,4'-dipyridyl (2) and a product formed after the sorption of pyridine, extracted from the surface of Pyshevsk montmorillonite (3).

Part of the Fe_2O_3 is directly contained in the mineral structure, while another part is found in the impurity-oxide film. The presence of iron oxide impurities in samples of laminar silicates is conveniently judged according to the presence of the band 2270 cm⁻¹ in the IR spectrum of acetonitrile adsorbed on them [10]. Experiments show that this maximum is observed in the spectrum of acetonitrile sorbed on Glukhovetsk kaolinite and is absent in the spectrum of Oglanly and Pyzhevsk montmorillonites with sorbed acetonitrile. Consequently, the oxide Fe_2O_3 is chiefly a component of the structure of the investigated montmorillonite samples, but is contained in the impurity-oxide film of kaolinite. Actually, extensive experience of the mineralogical study of kaolins [11] indicates that the Fe³⁺ ion registered in them by chemical methods belongs mainly to impurity oxides goethite and hematite.

An analysis of the data presented in Figs. 1 and 2 shows that the band in the region of 420 nm is especially distinct in the spectra of cation-substituted samples of Pyshevsk montmorillonite, which is characterized by the largest content of structural Fe^{3+} ions. Thus, it can be considered demonstrated that the cation radical of pyridine is formed chiefly in the sorption of molecules of this base on coordination-unsaturated Fe^{3+} cations of the side faces of the platelike particles of laminar silicates.

Cation radicals, being active particles, can initiate surface chemical reactions with the participation of molecules of sorbed pyridine. We identified the products of these reactions by the method of thin-layer chromatography and spectroscopy. For this a colored sample of the mineral was placed in a 50-mm test tube with ground joint and 10 ml of acetone was used to extract the products of chemical conversion of pyridine. The acetone extract obtained, in an amount of 50 μ l, was applied with a calibrated capillary onto plates with a thin layer of silica gel. The plate was developed in an eluent consisting of a mixture of hexane and diethylamine, taken in a 1:1 volume ratio and scanned on an Opton KM-3 spectrodensitometer (Federal Republic of Germany) at the 300 nm wavelength. The densitograms of the sample and presumed conversion products of pyridine (2,2'- and 4,4'-dipyridyls) are cited in Fig. 3. The R_f values (distance from the point of application to the center of the zone of the component, divided by the path traveled by the eluents on the plate) of the substances extracted from the surface of the sorbents and of the control substances coincide. The electronic diffuse reflection spectra of control spots of 2,2'- and 4,4'-dipyridyl and the extract were also taken. The results obtained confirm the presence of a mixture of dipyridyl isomers in the extract. Earlier [4] the formation only of 4,4'-dipyridyl in the chemisorption of pyridine by montmorillonite was registered according to the melting point of the extract product.

Pyridine is stable to the action of oxidizing agents. Only when it is heated to 300° C in the presence of FeCl₃ is it oxidized to a mixture of dipyridyls [12]. On the side faces of particles of natural laminar silicates, the oxidation of pyridine by coordination-unsaturated Fe³⁺ cations already occurs at room temperature. It evidently proceeds without an intermediate step of formation of the pyridine cation radical.

The electronic absorption spectra of 2,2'- and 4,4'-dipyridyl in neutral and acid solvents are characterized by absorption bands in the ultraviolet region at 280 and 250 nm, respectively. However, it is known [13, 14] that 2,2'-dipyridyl is a sensitive spectral indicator of Fe²⁺ ions. The complexes $[Fe(Dipy)_3]^{2+}$ are characterized by an absorption band in the region of 520 nm and a shoulder at 490 nm. On the side faces of crystals of montmorillon-



Fig. 4. Electronic diffuse reflection spectra of 2,2'-dipyridyl, sorbed on Ca forms of Oglanly (1) and Pyshevsk (2) montmorillonites and Glukhovetsk

(3) kaolinite.

ite and kaolinite, there is a small number of Fe^{2+} cations. Moreover, part of the Fe^{2+} cations are formed as a result of reduction of coordination-unsaturated Fe^{3+} ions in the formation of the cation radical of pyridine and dipyridyls. The molecules of 2,2'-dipyridyl may interact with divalent iron ions, forming colored complexes $[Fe(Dipy)_n]^{2+}$.

To prove this hypothesis, we studied the sorption of 2,2'-dipyridyl on various cationsubstituted forms of laminar silicates. As an example, Fig. 4 presents some of the spectral results obtained. The absorption bands of Ca-kaolinite with sorbed dipyridyl are close in position and intensity ratio to the maxima characteristic of the complexes $[Fe(Dipy)_3]^{2+}$ in aqueous solution. In the case of samples of montmorillonite with sorbed 2,2'-dipyridyl, a more long-wave absorption is superimposed upon the band in the region of 520-530 nm. As a result, a broad blurred band with maximum in the region of 550-560 nm is observed. Thus, the absorption at 490 and 520-530 nm in the spectra of laminar silicates with sorbed pyridine can be assigned to the surface complexes $[Fe(Dipy)_n]^{2+}$.

However, the possibility remains that the absorption in the visible part of the spectrum of samples of montmorillonite and kaolinite with sorbed pyridine is also due to electronic transitions in other surface chemical compounds. This is indicated, for example, by the appearance of the band 495 nm in the spectra of Ca and H forms of synthetic zeolites with sorbed pyridine [15]. On account of the low content of iron ions in the structure of zeolites, it can scarcely be ascribed to surface complexes $[Fe(Dipy)_n]^{2+}$. However, these complexes are colored red, and thus their spectral identification still does not explain the blue color of laminar silicates, which they frequently acquire after the sorption of pyridine.

The products of catalytic conversion of pyridine that absorb light in the region of 580-610 nm are responsible for the blue color of the sorbents. The most intense bands in this portion of the spectrum are possessed by Mg and Li samples of montmorillonite and kaolinite with sorbed pyridine. In the spectra of Ca, Sr, and K forms of Laminar silicates with sorbed pyridine, after their irradiation with a xenon lamp ($\lambda > 320$ nm), absorption also appears at 610 nm, determining the blue color of the sorbents. To explain these facts, let us recall that in the chemisorption of pyridine on the side faces of laminar silicates, 4,4'dipyridyl is formed together with 2,2'-dipyridyl. It is rather widely used in analytical chemistry as a redox indicator, which takes on a blue-violet color under the action of reducing agents [16].

Brönsted acid centers are present on the surface of laminar silicates. They are impurity-exchange protons, residual water molecules, highly polarized in the field of multiply

charged cations, and acid hydroxyl groups of the type of HO-Si-O-Al- [17, 18]. According

to the data of [17], the strength of the Brönsted centers on the surface of laminar silicates, depending on the kind of exchange cations, is equal to the acidity of 48-71% H₂SO₄. It is quite natural that the molecules of 4,4'-dipyridyl, possessing $PK_{\alpha} \sim 5.3$ [16], will ionize on the surface of laminar silicates under the influence of mobile protons. Twice-ionized 4,4'-dipyridyl, accepting an electron from the divalent iron ion, is converted to a semi-quinone on the surface of the sorbents:

For Ca, Sr, and K samples of laminar silicates, the formation of a semiquinone is initiated as a result of irradiation by the light of a xenon lamp. The presence of a mobile electron in the semiquinone is responsible for the high degree of coupling of its π -bonds and ultimately the absorption in the red region of the spectrum.

In the interaction of pyridine with Mg and Li forms of natural laminar silicates, the possibility of catalytic conversion of the molecules of this base according to a different mechanism, with the formation of heteroaromatic condensed systems, is also not excluded. This is indicated by the indistinct absorption in the region of 680 nm, which is more clearly manifested as a result of photoionization of sorbed pyridine (Fig. 2).

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