

Interactions of Co-Exchanged Montmorillonite with Pyridine, 4-Methyl- and 4-Ethylpyridine

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Thermal analysis (TG, DTG) and infrared absorption spectra were used to study the interactions of pyridine, 4-methylpyridine, and 4-ethylpyridine with Co-exchanged montmorillonite. It is shown that the bonds between the derivatives of pyridine and the montmorillonite exhibit predominantly the Lewis acid character. The total amount of pyridines inserted in the porous structure of montmorillonite increases in the following sequence: unsubstituted, 4-methyl-, 4-ethylpyridine.

One of the characteristic features of dioctahedral smectites is their layered structure. The layers are formed by two tetrahedral sheets linked with an octahedral sheet. Isomorphous substitution in the octahedron and/or tetrahedron generates a negative charge on the layers, which is balanced by hydrated exchangeable cations in the interlayer, mostly Ca^{2+} , Mg^{2+} , and Na^+ in natural samples (but also Fe^{2+} , Co^{2+} , Ni^{2+} , and Cu^{2+} ions) [1]. Polar organic molecules (as pyridine) can replace the water which normally occupies the interlayer spaces in the montmorillonite.

The clay minerals with layered structure have considerable practical importance. They act as efficient catalysts for a variety of organic reactions [2–5]. Montmorillonites are also important in areas of environmental concern, and for such applications a precise knowledge of the interaction mechanisms between clay minerals and metal cations, such as Cu(II), Cu(I), Cd(II), Zn(II), *etc.*, is greatly desirable as these cations are often present in various forms in polluted soils [6].

Much interest was devoted to the interactions between clays and organic materials with the purpose of determining the structure and stability of the organic clay complexes and the types of bonds between clay component and the adsorbed organic species. Since the clay surface and its interlayer space are populated by Brønsted and Lewis acids and basic sites, the principal interactions between the clay and the adsorbed organic compounds are of the acid-base type [7]. In order to examine the type of acid sites in clays, thermal curves and IR spectroscopy were applied for the exam-

ination of pyridine and pyridine derivatives desorption products [8–10]. The differences in desorption characteristics are attributed to different electronic properties, namely to the $\text{p}K_{\text{b}}$ values of desorbed bases [9, 10].

In this paper thermal analyses (TG, DTG) and infrared absorption spectra (IR) have been used to study the release of pyridine, 4-methylpyridine, and 4-ethylpyridine from Co-exchanged montmorillonite upon heating, in order to evaluate the importance not only of electronic properties of studied bases, but also of their steric properties. In this connection we have directed our attention to the investigation, whether pyridine, 4-methyl- and 4-ethylpyridine occupy in Co^{2+} -exchanged montmorillonite predominantly Lewis or Brønsted acid sites.

DTG curves of Co^{2+} -exchanged montmorillonite (*I*) and DTG curves of its preparations saturated by pyridine derivatives *II–IV* (see Experimental) are shown in Fig. 1. Thermal analysis results (TG, DTG) for all studied samples are summarized in Table 1. The thermal decomposition of sample *I* proceeds under dynamic conditions and in the temperature interval 20–700 °C in two distinct steps. The first step can be assigned to the release of adsorbed water molecules with maximum on the DTG curves at ≈ 103 °C (Table 1), while the second one is connected with a release of water molecules from hydroxide groups (temperatures for maxima of peaks on DTG curves at about 650 °C). The pyridines-exchanged montmorillonites *II–IV* exhibit three desorption peaks with maxima in the regions 64–67 °C, 370–442 °C, and 627–637 °C, respectively

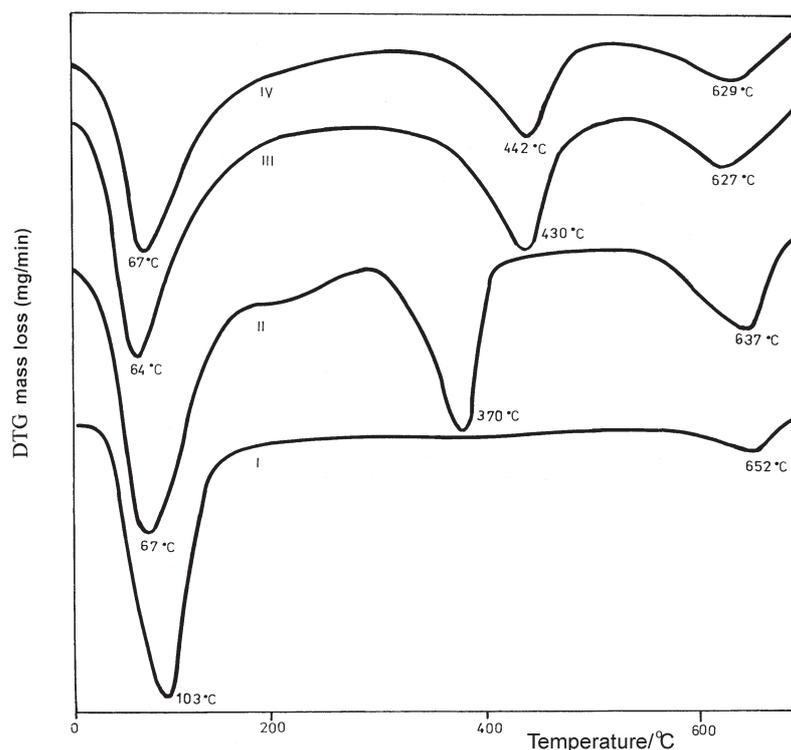


Fig. 1. DTG curves of I–IV.

Table 1. Thermal Analysis Results for the Release of Pyridines from Co^{2+} -Exchanged Montmorillonites (200–700 °C)

| Sample | TG: $\Delta w/\%$ | | | DTG: $\theta_p/^\circ\text{C}$ | | |
|--------|-------------------|-----|-----|--------------------------------|-----|-----|
| | 1 | 2 | 3 | 1 | 2 | 3 |
| I | 15.0 | – | 4.4 | 103 | – | 652 |
| II | 5.3 | 6.4 | 3.7 | 67 | 370 | 637 |
| III | 6.2 | 6.3 | 3.1 | 64 | 430 | 627 |
| IV | 7.3 | 6.2 | 2.9 | 67 | 442 | 629 |

Table 2. Representative Diffraction and IR Spectral Data of Studied Samples I–IV

| Sample | $2\theta/^\circ$ | $\tilde{\nu}$ (Maxima of absorption bands)/ cm^{-1} |
|--------|------------------|--|
| I | 5.84 | – 1632 – |
| II | 6.72 | 1641, 1620 (sh), 1551, 1492, 1448 |
| III | 6.09 | 1645, 1622, 1550 (sh), 1512, 1451 |
| IV | 6.36 | 1643, 1627, 1570, 1560, 1508, 1458 |

(Table 1). In accordance with Breen [9, 10] the first and second peaks correspond to the release of physically sorbed and chemically bonded pyridines, while the third one may be assigned to lattice dehydroxylation of the samples.

The samples of adsorbed pyridine exhibited IR absorption bands that were assigned to physisorbed pyridine (1434 cm^{-1} and 1485 cm^{-1}), hydrogen-bonded pyridine (753 cm^{-1} and 1590 cm^{-1}), Lewis acid-bound pyridine (1445 cm^{-1} , 1485 cm^{-1} , 1578 cm^{-1} , 1590 cm^{-1} , and 1613 cm^{-1}), and the pyridine cation (1485 cm^{-1} , 1540 cm^{-1} , 1606 cm^{-1} , and 1635 cm^{-1}) [8–11].

Representative data from IR spectra of the studied samples are presented in Table 2. The significant difference between I and adsorption products II–IV can be observed in the region $1400\text{--}1700\text{ cm}^{-1}$. Sample I showed one band in the H_2O deformation region at $\approx 1632\text{--}1637\text{ cm}^{-1}$ assigned to “bound water” [7].

The samples with pyridine derivatives exhibit in this region a double peak at $\approx 1640\text{ cm}^{-1}$ and $\approx 1620\text{ cm}^{-1}$. The peaks at $\approx 1448\text{--}1458\text{ cm}^{-1}$, $1492\text{--}1512\text{ cm}^{-1}$, $1550\text{--}1570\text{ cm}^{-1}$, and $1620\text{--}1627\text{ cm}^{-1}$ may be attributed to Lewis acid-bound pyridine. Since the band at $\approx 1595\text{ cm}^{-1}$ [12] has not been observed, the occurrence of R-pyridine hydrogen bonded to water in the studied systems is not probable. This is in agreement with literature data. Breen [9] has shown that a prevailing feature of IR spectra of pyridine M^{2+} -montmorillonites ($\text{M}^{2+} = \text{Ni}, \text{Co}$) is the overall dominance of bands associated with Lewis acid-bound pyridine.

Selected diffraction patterns of the studied samples are shown in Fig. 2. The diffraction at $2\theta = 5.84^\circ$ dominates the X-ray powder pattern of the Co-MMT. The changes of this diffraction in the powder pattern of the samples II–IV prove the presence of R in the interlayer spaces. The corresponding interlayer distance

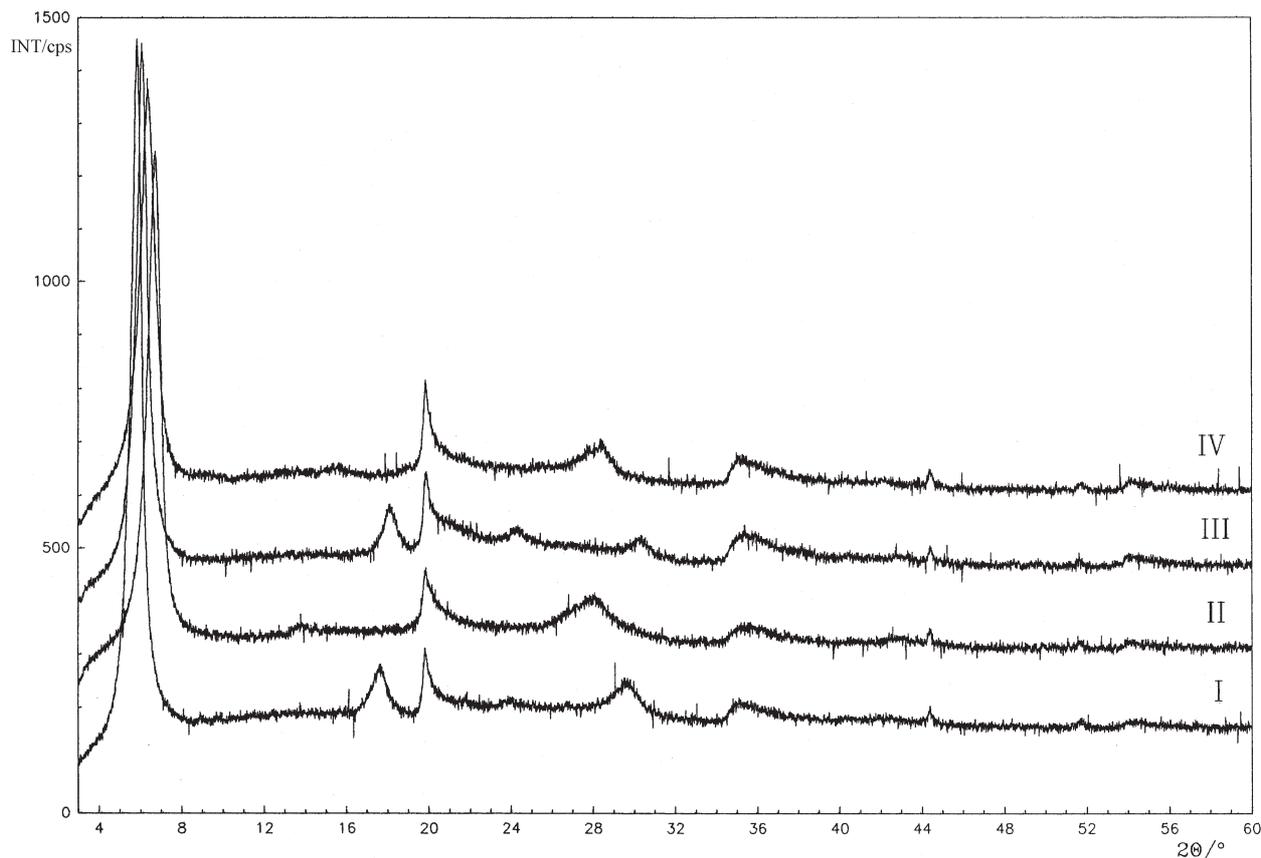


Fig. 2. Selected diffraction patterns of the studied samples *I–IV*.

decreases (2θ values increase) in the sequence: *I*, *III*, *IV*, *II* (Table 2).

In conclusion we can state that the pyridine and pyridine derivatives may be physically sorbed to the Co-exchanged montmorillonite but the principal interactions between them are of the acid-base type. In the interlayer space of montmorillonite water molecules which are coordinated to exchangeable metallic cations (M^{n+}) serve as proton donors (Brønsted acid). The organic base may be protonated by a proton from a water molecule, thus gaining a positive charge. The exchangeable cations may also serve as Lewis acids and organic bases become coordinated directly to the cation M^{n+} .

As shown from IR spectra (Table 2) the major type of acid site in *I* is of electron-accepting or Lewis acid character. This is in marked contrast to the predominantly Brønsted and/or Brønsted and Lewis character of trivalent cation-exchanged clays [10].

The thermal studies indicated (Fig. 1, Table 1) that there are little differences in the mass losses and desorption temperatures of studied samples *II–IV* but the total amount of the pyridines inserted in the porous structure of Co-exchanged montmorillonite in-

creases in the following sequence: unsubstituted, 4-methyl-, 4-ethylpyridine.

EXPERIMENTAL

Less than 2 μm -fraction of bentonite from Jelšovský Potok (bentonite deposit in the central part of Slovakia) was separated from a bulk sample and converted into the monoionic Ca-form using standard methods [8]. The structural formula as calculated from the chemical analysis of the fine fraction is: $\text{Ca}_{0.48}(\text{Si}_{7.59}\text{Al}_{0.41})(\text{Al}_{3.06}\text{F}_{0.34}\text{Mg}_{0.63})(\text{OH})_4\text{O}_{20}$.

The monoionic form Co-exchanged montmorillonite was prepared from the Ca-form (3g) by the addition of a CoCl_2 solution (400 cm^3 , $c = 1 \text{ mol dm}^{-3}$) and the mixture was stirred for a short time and left to stand for 24 h. After decantation CoCl_2 solution was added again to the solid phase, stirred and left to stand as previously. This procedure was repeated four times. The solid product was then washed by water in order to remove the Cl^- anions and finally dried at 60 °C. A thin layer ($\approx 250 \text{ mg}$) of monoionic form was exposed to pyridine vapours for 72 h at room temperature. The same procedure was performed with 4-methyl- and 4-ethylpyridine (products *II*, *III*, and *IV*, respectively).

The analytical methods used have been described elsewhere [7]. The thermal properties were studied with a Derivatograph OD 102 (MOM Budapest). The measurements were carried out in nitrogen using a platinum crucible. Sample masses of about 30–34 mg and a rate of temperature increase of $10\text{ }^{\circ}\text{C min}^{-1}$ were used in thermal decompositions. The exact masses of samples are given at the corresponding figures.

The infrared spectra were recorded at room temperature with a Nicolet MAGNA 750 FTIR spectrometer in the range of $400\text{--}4000\text{ cm}^{-1}$. Powder diffraction patterns were taken on an automated Brac—Brentano Dron UM-1 diffractometer with $\text{CuK}\alpha$ radiation.

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REFERENCES

1. Madejová, J., Arvaiová, B., and Komadel, P., *Spectrochim. Acta A55*, 2467 (1999).
2. Thomas, J. M., *Sheet Silicate Intercalates: New Agents for Unusual Chemical Conversions in Intercalation Chemistry*. Academic Press, New York, 1982.
3. Ballantine, J. A., Davies, M. E., Purnell, J. H., Rayanakorn, M., and Thomas, J. M., *J. Chem. Soc., Chem. Commun.* 1981, 427.
4. Gregory, R., Smith, D. J. H., and Westlake, D. J., *Clay Miner.* 18, 431 (1983).
5. Ballantine, J. A., Davies, M. E., Purnell, J. H., Rayanakorn, M., Thomas, J. M., and Williams, K. J., *J. Chem. Soc., Chem. Commun.* 1981, 8.
6. Baker, D. E. and Serft, J. P., in *Heavy Metals in Soils*. (Alloway, B. J., Editor.) P. 179. Blackie Academic and Professional, London, 1995.
7. Yariv, S., *Thermochim. Acta* 274, 1 (1996).
8. Jóna, E., Kubranová, M., Sirota, A., and Kopcová, M., *J. Therm. Anal. Cal.* 63, 807 (2001).
9. Breen, C., Deane, A. T., and Flynn, J. J., *Clay Miner.* 22, 169 (1987).
10. Breen, C., *Clay Miner.* 26, 473 (1991).
11. Ward, J. W., *J. Colloid Interface Sci.* 28, 269 (1968).
12. Farmer, V. C. and Mortland, M. M., *J. Chem. Soc. A* 1966, 344.