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NANOMATERIALS ON THE BASIS OF LAYERED SILICATES

ABSTRACT

Thermal analysis (TG, DTG) and infrared spectroscopy were used to study the interactions of 4-methylpyridine (4-Mepy), 4-ethylpyridine (4-Etpy) and 4-hydroxypyridine (4-OHpy) with M^{2+} -exchanged montmorillonite ($M = \text{Co, Ni, Cu}$). It is shown that the bonds between the derivatives of pyridine and transition metal ions in montmorillonites (MMT) exhibit predominantly the Lewis acid character while in 4-OHpy/ M^{2+} -MMT Brønstedt-bound 4-OHpy molecules can be considered.

The present results reveal that M^{2+} -exchanged montmorillonites are suitable for the incorporation of pyridine derivatives in their layered structure and the formation of new clay-coordination compounds.

INTRODUCTION

During the last decades much interest was devoted to the study of the layered silicates. This study is connected with practical applications of these materials, because layer clay minerals act as efficient catalysts for variety of organic reactions and play also an important role as adsorbents of hazardous organic pollutants in the soil. The immobilization and detoxification of hazardous substances with clay minerals (especially montmorillonites) represent wide area for research. In this context it is important to study the nature of interactions occurring between organic compounds and montmorillonites [1, 2].

Montmorillonite (MMT) belongs to the group of expanding layered lattice silicate minerals known as smectites, having the layers formed as two tetrahedral sheets linked with an

octahedral one. Negative charge of the layers is balanced by hydrated exchangeable cations [3]. Polar organic molecules (e.g. pyridine derivatives) can replace the water molecules which as a rule occupy the interlayer spaces in the montmorillonite. In introducing transition metal ions and adding suitable ligands even clay-compounds may be formed in the interlayers of MMT. Since the montmorillonite surface and its interlayer space are populated by Brösted and/or Lewis acid sites, the principal interactions between the clay and the organic compounds are those of the acid–base type [4–6].

Many authors investigated heterocyclic compounds with pyridine ring due to their structural and biological properties and examined them as ligands in solid coordination compounds [7–9]. In this paper thermal analysis (TG, DTG and DTA) and infrared absorption spectra have been used to study the type of interactions between transition metal ions (Co^{2+} , Ni^{2+} , Cu^{2+}) and pyridine derivatives (4-R pyridine, R = CH_3 , C_2H_5 , OH) in montmorillonite.

The presented results reveal that M^{2+} -exchanged montmorillonite (M = Co, Ni, Cu) has provided suitable reaction media for the incorporation of neutral organic bases (4-Rpy) in its layer structure [10–14].

EXPERIMENTAL

Synthesis of the samples

Less than 2 μm -fraction of Jelšovský Potok was separated from a bulk sample and converted into the monoionic Ca-form using standard methods [10]. The structural formula as calculated from the chemical analysis of the fine fraction is: $\text{Ca}_{0,48}(\text{Si}_{7,59}\text{Al}_{0,41})(\text{Al}_{3,06}\text{Fe}_{0,34}\text{Mg}_{0,63})(\text{OH})_4\text{O}_{20}$.

The M^{2+} -exchanged montmorillonites (M = Co, Ni and Cu) were prepared from the Ca-form (3 g) by the addition of a MCl_2 solution (450 cm^3 , $c = 1 \text{ mol}\cdot\text{dm}^{-3}$) and the mixture was stirred for a short while and left to stand for 24 h. After decantation MCl_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 forms was exposed to 4-Rpyridine (R = methyl, ethyl) vapours for 72 h at room temperature.

In case of solid 4-OHpy, the monoionic forms M^{2+} -MMT were added to 5 % of the compound. The mixture was stirred 1 h and left to stand 3 h. This procedure was repeated

three times. On the next day the solid products 4-OHpy/M²⁺-MMT were washed with ethanol (ten times) and dried at 60 °C.

Analytical methods and equipment

The analytical methods used have been described elsewhere [10]. The thermal properties were studied with a TA Instrument SDT 2960. The measurements were carried out in air using a platinum crucible. A sample mass of 20–25 mg and heating rate 10 °C.min⁻¹ were used in particular thermal decomposition. The X-ray diffraction profiles for pressed powder samples were recorded on a Philips PW 1050 diffractometer 2° (2 Θ) min⁻¹ using CuK α radiation. The infrared absorption spectra were recorded with Nicolet Magna 750 Fourier Transform IR spectrometer in the range of 4000–400 cm⁻¹.

RESULTS AND DISCUSSION

As reported previously [11–14] thermal analysis combined with measuring of infrared spectra can provide a precious information about the character of interactions between the adsorbed pyridine derivatives and monoionic montmorillonite containing a metal ion in its interlayer spaces.

Thermal data from TG and DTG curves of studies samples I–XII are summarised in Table 1. The thermal decomposition of M²⁺-MMT (samples I, V, IX) proceeds under dynamic conditions in the temperature interval 20–700°C in two distinct steps. The first step can be assigned to the release of adsorbed water molecules while the second one is connected with a lattice dehydroxylation .

Three or four steps of decomposition of 4-Rpy/ M²⁺-MMT are observed in the temperature interval under study for samples II–IV, VI–VIII and X–XII. The first step can be assigned to the desorption of 4-Rpy while the last one corresponds to the lattice dehydroxylation. The second peaks for samples II, III, VI, VII and X, XI and the second and third ones found for samples IV, VIII and XII can be assigned to release of chemically bonded 4-Rpy [5, 6, 10, 15].

Sample	TG: Δm / %			DTG: T_p / °C		
	Steps					
	1	2	3			
Co-MMT(I)	15	–	4,4	103	–	652
4-Mepy/Co-MMT(II)	6,2	6,3	3,1	64	430	627
4-Etpy/Co-MMT(III)	7,3	6,2	2,9	67	442	629
4-OHpy/Co-MMT(IV)	6,5	3,5; 1,9	3,8	67	380; 470	610
Ni-MMT(V)	16,6	–	5,3	82	–	656
4-Mepy/Ni-MMT(VI)	5,2	8,7	3,4	46	420	640
4-Etpy/Ni-MMT(VII)	3,2	11,3	3,1	52	407	636
4-OHpy/Ni-MMT(VIII)	6,3	3,7; 2,7	3,2	62	380; 470	610
Cu-MMT(IX)	13,2	–	4,6	68	–	640
4-Mepy/Cu-MMT(X)	3,1	7,8	4,6	50	380	612
4-Etpy/Cu-MMT(XI)	2,4	8,1	4,4	44	380	605
4-OHpy/Cu-MMT(XII)	6,1	1,8; 2,9	5,5	48	280; 380	650

Table 1. Thermal analysis results for the release of pyridine derivatives from Co²⁺-, Ni²⁺ and Cu²⁺-exchanged montmorillonites (20-700°C)

The data from infrared spectra are given in Table 2. The significant difference between pure M²⁺-MMT (I, V, IX) and the products (II–IV, VI–VIII, X–XII) can be observed in the region 1700–1400 cm⁻¹. Whereas samples I, V and IX show only one sharp band at ~1632–1635 cm⁻¹ assigned to the deformation vibration of H–O–H groups [16], the samples with 4-Rpy exhibit in this region several peaks of 4-Rpy in the interval 1647–1622, 1520, 1512–1508 and 1451–1435 cm⁻¹. It is known [17–19], that the peak at ~1600 cm⁻¹, attributed to the ring vibration in the pyridine molecules (for example 4-Mepy shows peak at 1604 cm⁻¹ [20]) shifts to higher frequencies upon complex formation. The shift of this peak to about 1647–1622 cm⁻¹ may support the conclusion on the formation of coordination bond between M²⁺ central atoms and the nitrogen atom of the heterocyclic ring in these samples. This assertion also supports the presence of the „diagnostic“ Lewis peak at ~1451–1435 cm⁻¹. Samples containing OH group in 4-position on the pyridine ring, show two peaks in the studied region at ~1647–1642 cm⁻¹ and 1520 cm⁻¹ (Table 2).

Sample	$\tilde{\nu}$ (maxima of absorption bands)/cm ⁻¹			
I	1632 (vs)	–	–	–
II	1645 (s), 1622 (sh)	–	1512 (w)	1451(w)
III	1642 (s), 1627 (vs)	1558 (w)	1508(w)	1462(w),1436(w)
IV	1643 (vs)	–	1520 (vs)	–
V	1634(vs)	–	–	–
VI	1644 (s), 1622 (vs)	–	1509 (s)	1441(s)
VII	1642 (s), 1622 (vs)	1558 (vw)	1508 (w)	1439 (s)
VIII	1648 (vs)	–	1520 (vs)	–
IX	1635(vs)	–	–	–
X	1642 (s), 1624 (vs)	–	1510 (s)	1439(s)
XI	1647 (sh), 1622 (vs)	1559 (w)	1508 (w)	1435 (s)
XII	1645 (vs)	–	1520 (vs)	–

Table 2. Representative infrared spectral data of studied samples I-IX (1400 – 1700 cm⁻¹).
(vs – very strong, w – weak, sh – shoulder)

The first peak may be assigned both to deformation vibration of H₂O molecules and the ring vibration of pyridine molecules, and thus Lewis-bound pyridine in these samples cannot be excluded. Moreover, a peak near 1520 cm⁻¹ suggests also the presence of some Brönsted-bound pyridine molecules [13]. This assumption can also explain the occurrence of two peaks on TG and DTG curves for samples with 4-OHpy (Table 1).

CONCLUSIONS

The presented results reveal that M²⁺-exchanged montmorillonite (M = Co, Ni, Cu) has provided suitable reaction media for the incorporation of neutral organic bases (4-Rpy) in its layered structure.

The thermal effects accompanying the escape of 4-Rpy from obtained products in the temperature interval 20–700 °C indicate that the stoichiometry of thermal decomposition is different (samples containing 4-OHpy exhibit in this region four effects in contrast to the 4-Me and 4-Etpy/M²⁺-MMT).

The infrared spectra show that bonds between 4-Rpy (R = Me, Et) and M²⁺-exchanged montmorillonites predominantly exhibit Lewis acid character with exception of samples with

4–OHpy in which we consider Brönsted type of interactions. Thus, the influence of different substituents on the pyridine ring on the thermal and spectral properties of studied samples is evident.

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