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THERMAL PROPERTIES OF Co-, Ni- AND Cu-EXCHANGED MONTMORILLONITE WITH 3-HYDROXYPYRIDINE

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Abstract

Thermal analysis (TG, DTG), powder diffraction analysis (RTG) and infrared absorption spectra (IR spectra) were used to study of release of 3-hydroxypyridine (3-OHpy) from Co-, Ni- and Cu-exchanged montmorillonite (Co-MMT, Ni-MMT, Cu-MMT). It was found that release of 3-OHpy under heating from Co- and Ni-MMT proceeds in three distinct steps while from Cu-MMT in four steps. The first step can be assigned to the release of physically sorbed 3-OHpy while the last one corresponds to the lattice dehydroxylation. The second step (Co-, Ni-MMT) and/or second and third steps (Cu-MMT) can be assigned to release of chemically bonded 3-OHpy. This investigation shows that studied exchanged montmorillonites predominantly exhibit Lewis acid character.

Keywords: Co-, Ni- and Cu-exchanged montmorillonite, 3-hydroxypyridine

Introduction

Montmorillonite (MMT) belongs to the groups of expanding layer – lattice silicate minerals known as smectite. The layers are formed by two tetrahedral sheets linked with an octahedral sheet. A negative charge on the layers is balanced by hydrated exchangeable cations [1]. Polar organic molecules (as pyridine derivatives) can replace the water which normally occupies the interlayer spaces in the montmorillonite. By introducing transition metal ions into the layer of MMT and then adding suitable ligands, complexes may be formed [2]. The behaviour of the formed complexes is as a rule significantly influenced by the unique environment of the silicate surface. Since the montmorillonite surface and its interlayer space are populated by Brönsted and/or Lewis acidic sites the principal interactions between the clay and the organic compounds are of the acid–base type [3]. Some methods such thermogravimetry, derivative thermogravimetry and infrared spec-

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troscopy were applied to obtain information on the thermal properties and on the type of interaction between adsorbed species and functional sites on the clay surface. It has been shown [4, 5] that a prevail feature of infrared spectra of R–py/M^{2+}- MMT (*R*=H, methyl, ethyl and *M*=Co, Ni) is the overall dominance of bands associated with Lewis bound R-py in contrast to the result of identical studies on Al^{3+}, Fe^{3+} and Cr^{3+}-exchanged montmorillonite in which all three cation exchanged forms exhibited intense Brönsted bound pyridine band at 1540 cm^{-1}.

In this paper thermal analysis (TG, DTG), powder diffraction analysis (RTG) and infrared spectra (IR spectra) have been used to study the release of 3-hydroxypyridine (3-OHpy) from Co-, Ni- and Cu-exchanged MMT in order to evaluate the importance not only different transition metal ions but also different substituent on pyridine ring (OH groups in comparison with methyl and ethyl groups [5, 6]).

Experimental

Syntheses of the samples

Less than 2 μm fraction of bentonite from Jelšový 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 [5]. The crystallochemical formula of Ca-MMT is as follows: $Ca_{0.48}\,(Si_{7.59}Al_{0.41})(Al_{3.06}F_{0.34}Mg_{0.63})(OH)_4O_{20}$.

The monoionic form of M^{2+}-MMT (*M*=Co, Ni, Cu) (I–III) was prepared from the Ca-MMT. 400 cm^3 of a MCl_2 solution (c=1 mol dm^{-3}) was added to 3 g of Ca-MMT, the mixture was stirred for a short time 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 with water in order to remove the Cl^- anions and finally dried at 60°C.

The monoionic forms Co-, Ni- and Cu-MMT were added to 5% solution of 3-hydroxypyridine. The mixture was stirred 1 h and left to stand 3 h. This procedure was repeated three times. On the second day the solid products 3-OHpy/Co-MMT (IV), 3-OHpy/Ni-MMT (V) and 3-OHpy/Cu-MMT (VI) were washed with ethanol (ten times) and dried at 60°C.

Analytical methods and equipment

The analytical methods used have been described elsewhere [7]. The thermal properties were studied with a TA Instruments 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 decompositions. The X-ray diffraction profiles for pressed powder samples were recorded on a Philips PW 1050 diffractometer at 2° (2Θ) min^{-1} using CuK_α radiation. The infrared absorption spectra were recorded with a Nicolet Magna 750 Fourier Transform IR spectrometer in the range of 4000–400 cm^{-1}.

Results and discussion

Thermal analysis

DTG curves of Co^{2+}-, Ni^{2+}- and Cu^{2+}-exchanged montmorillonite (I–III) and intercalation products with 3-hydroxypyridine (IV–VI) are shown in Figs 1 and 2. Thermal data from TG and DTG curves of studied samples are summarised in Table 1.

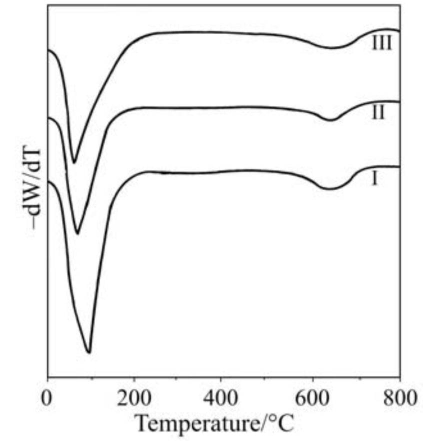

Fig. 1 DTG curves of Co-MMT (I), Ni-MMT (II) and Cu-MMT (III)

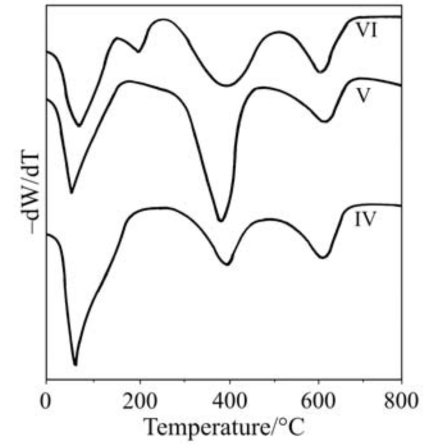

Fig. 2 DTG curves of 3-OHpy/Co-MMT (IV), 3-OHpy/Ni-MMT (V) and 3-OHpy/Cu-MMT (VI)

The thermal decomposition of samples I–III proceeds under dynamic conditions and in temperature interval 20–800°C in two distinct steps. The first step can be assigned to the release of adsorbed water molecules with maximum on the DTG curve at ~80–100°C (Table 1) while the second step is connected with a release of water molecules from hydroxide groups (temperatures for maxima of peaks, T_p, on DTG curve at about 79–103°C).

Table 1 Thermal analysis results for studied samples

Sample	TG			DTG
	steps	Δm/%	released component	T_p/°C
Co-MMT (I)	1.	15.5	adsorbed H_2O	103
	2.	4.4	structural H_2O	652
Ni-MMT (II)	1.	18.3	adsorbed H_2O	79
	2.	5.2	structural H_2O	656
Cu-MMT (III)	1.	11.3	adsorbed H_2O	83
	2.	5.5	structural H_2O	640
3-OHpy/Co-MMT (IV)	1.	8.2	adsorbed 3-OHpy	68
	2.	5.8	bonded* 3-OHpy	450
	3.	4.1	structural H_2O	620
3-OHpy/Ni-MMT (V)	1.	6	adsorbed 3-OHpy	61
	2.	9.4	bonded 3-OHpy	380
	3.	3.8	structural H_2O	625
3-OHpy/Cu-MMT (VI)	1.	5.8	adsorbed 3-OHpy	80
	2.	2.7	bonded 3-OHpy	220
	3.	7.9	bonded 3-OHpy	410
	4.	4.3	structural H_2O	620

*chemically bonded

The intercalation products with 3-hydroxypyridine exhibit three steps in studied temperature interval (samples IV and V) and/or four steps (sample VI). The first step can be assigned to the physically sorbed 3-OHpy while the last one corresponds to the lattice dehydroxylation. The second step (IV, V) and/or second and third steps (VI) in temperature interval 220–410°C can be assigned to the release of chemically bonded 3-OHpy [4, 8].

The structural changes and the type of chemical bond of 3-OHpy in intercalation products have been studied by means of diffraction and spectral analysis.

Diffraction patterns and IR spectroscopy

Selected powder diffraction patterns of the studied samples are shown in Fig. 3 and obtained results are summarized in Table 2. The diffraction at d_{001}=12.7–15.3 Å dominates the X-ray powder pattern of the Co^{2+}, Ni^{2+} and Cu^{2+}-exchanged montmorillonite (samples I–III). The changes of this diffraction in the powder pattern of the intercalation products (samples IV–VI) indicate the incorporation of the 3-OHpy in their layer structure.

Table 2 Representative interlayer distances (d_{001}) and maxima of IR absorption bands (1400–1700 cm^{-1}) of studied samples

Sample	d_{001}/Å	Maxima of absorption bands/cm^{-1}					
		δ(H–O–H)	ν(ring of py)				
I	15.3	1637	–				
II	15.3	1634	–				
III	12.7	1638	–				
3-OHpy	–	–	1608	1583	1558	1506(sh)	1489
IV	12.8	–	1629	1571	–	1553(sh)	1488
V	13.0	–	1629	1572	–	–	1492
VI	12.6	–	1629	1571	–	1556(sh)	1488

The results of infrared spectroscopy are given in Table 2. The significant difference between pure M^{2+}-MMT (I–III) and the intercalated products (IV–VI) can be observed in the region 1700–1400 cm^{-1}. Whereas samples I–III produces one strong, sharp absorption band at ca 1634–1637 cm^{-1} assigned to deformation vibration of H–O–H groups [9], the intercalation species (IV–VI) exhibit in this region several peaks of 3-OHpy at ca 1629, 1571–1572 and 1488–1492 cm^{-1}. Pure 3-OHpy exhibits in the studied region four strong peaks at ca 1608, 1583, 1558 and 1489 cm^{-1}. The

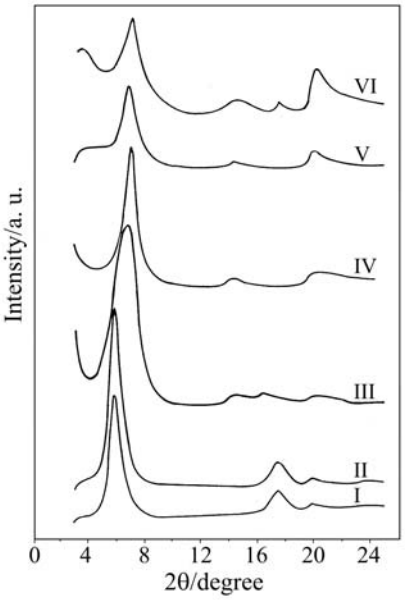

Fig. 3 Powder diffractograms of Co-MMT (I), Ni-MMT (II), Cu-MMT (III), 3-OHpy/Co-MMT (IV), 3-OHpy/Ni-MMT (V) and 3-OHpy/Cu-MMT (VI)

peak at 1608 cm^{-1} (attributed to the stretching vibration of the C=N group in the pyridine ring) shifts to higher freqencies upon complex formation. The shift of this peak to ca 1629 cm^{-1} in intercalates samples IV–VI may suggest the formation of coordination bond between the M^{2+} and nitrogen atom of heterocyclic ring [10–13]. Since the bands at 1595 and 1540 cm^{-1} have not been observed, the occurrence of 3-OHpy hydrogen bound to water and/or protonated by accepting of proton from a water molecule are not probable [14]. Then we assume that the major type of acid site in the 3-OHpy/M^{2+}-exchanged montmorillonite (M=Co, Ni, Cu) is of electron accepting or Lewis acid character. The similar results have been observed for Co^{2+}- and Ni^{2+}-exchanged montmorillonite with 4-methylpyridine and 4-ethylpyridine [5, 6].

Conclusions

The presented results revealed that montmorillonite and its exchanged species (M^{2+}-MMT, M=Co, Ni, Cu) have provided suitable reaction media for the incorporation of organic base (3-hydroxypyridine) in their porous structure.

The thermal effects accompanying the escape of 3-OHpy from intercalation products in the temperature interval 20–800°C indicate that the stoichiometry of thermal decomposition is different for studied samples. TG and DTG curves of 3-OHpy/Cu-MMT exhibit in this region four steps (Table 1) in contrast to the Co- and Ni-species. Then the influence of the transition metal ions is evident.

The total amounts of the 3-OHpy inserted in the porous structure of the studied species are increasing in the following sequence (Table 1):

$$\text{3-OHpy/Co}^{2+}\text{-MMT} < \text{3-OHpy/Ni}^{2+}\text{-MMT} < \text{3-OHpy/Cu}^{2+}\text{-MMT}$$

The changes in the powder diffraction patterns of the intercalation species (3-OHpy/M^{2+}-MMT) in comparison with M^{2+}-MMT indicate the presence of 3-OH pyridine in the interlayer space.

The infrared spectra of studied samples are equal and show that the bonds between 3-OHpy and all M^{2+}-exchanged montmorillonites predominantly exibit Lewis acid character. Then we assume that the differences in stoichiometry of thermal decomposition of intercalation products are not connected with different type of bond of 3-OHpy. It can be expected that these and similar intercalation compounds will exhibit specific properties from the point of view of adsorption and catalysis [15].

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