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THERMAL AND INFRARED STUDY OF DESORPTION OF PYRIDINE AND PYRIDINE DERIVATIVES FROM Ni-EXCHANGED MONTMORILLONITE

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Abstract

Thermal analysis (TG, DTG) and infrared absorption spectra were used to study desorption of pyridine (py), 4-methylpyridine (4-Mepy) and 4-ethylpyridine (4-Etpy) from Ni(II)-exchanged montmorillonite (Ni-MMT). It is shown that the bonds between the derivatives of pyridine (R-py) and the montmorillonite exhibit predominantly Lewis acid character. The thermal stability of studied samples and the total amounts of R-py inserted in the porous structure of Ni-MMT increase in the following sequence: py/Ni-MMT<4-Mepy/Ni-MMT<4-Etpy/Ni-MMT, i. e. the influence of the substituent on the pyridine ring is evident.

Keywords: desorption of pyridine derivatives, infrared spectra, Ni(II)-montmorillonite, thermal study

Introduction

In a review Thomas [1] has shown that the clay minerals act as efficient catalysts for a variety of organic reactions. It has been accepted that the Brönsted acidity which gives rise to the catalytic activity of clay is derived from the polarization of solvent water molecules by the small highly charged interlayer cations. Environmental chemistry is another region where clay minerals play an important role and information on the adsorption of hazardous organic pollutants is essential for forecasting the migration of these molecules through soils and sediments and in the running water [2, 3]. This information is also important for industrial problems since clay minerals are used as filters in some industrial processes.

During the last decades much interest was devoted to the interactions between clays and organic materials with the purpose of determining the structure and stability of the organo-clay complexes and the types of bonds between clay component and the adsorbed organic species. Since the clay surface and its interlayer space are popu-

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lated by Brönsted and Lewis acidic and basic sites the principal interactions between the clay and the absorbed organic compounds are of the acid-base type [4].

Some methods such as thermo-IR-spectroscopy analysis, were applied to obtain information on the adsorption mechanism of organic compounds by clay minerals and on the type of bond between adsorbed species and functional sites on the clay surface [4]. In order to examine the type of acid sites in clays, derivative curves were applied for the study of desorption of bases, as demonstrated for *n*-butylamine, cyclohexylamine and pyridine [5–7]. Desorption of cyclohexylamine from Brönsted sites proceeds over a short temperature interval whereas that of pyridine is more prolonged [6]. In the contrary to the desorption properties of cyclohexylamine, desorption of pyridine from the Lewis sites is rapid and results in a sharp maximum in the derivative curve. These differences in desorption characteristics are attributed to different electronic properties, namely to the pK_b values of desorbed bases [5,7]. While cyclohexylamine (pK_b=3.3) will interact with both weak and strong sites, a weak base such as pyridine (pK_b=8.8) will interact with strong acid sites only.

In this paper thermal analyses (TG, DTG) and infrared absorption (IR) spectra have been used to study the desorption of pyridine and its derivatives from Ni(II)-exchanged montmorillonite in order to evaluate the importance not only electronic but also the steric properties of desorbed bases. In this connection we have focused our attention on pyridine (py), 4-methylpyridine (4-Mepy) and 4-ethylpyridine (4-Etpy).

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 [8]. The crystallochemical formula of Ca-MMT is as follows: $Ca_{0.48}(Si_{7.59}Al_{0.41})(Al_{3.06}F_{0.34}Mg_{0.63})(OH)_4 O_{20}$.

The monoionic form of Ni-MMT was prepared from of the Ca-MMT in a way that 400 cm^3 of a $NiCl_2$ solution (c=1 mol dm^{-3}) were added to 3 g of Ca-MMT, the mixture was stirred for a short time and left to stand for 24 h. After decantation $NiCl_2$ 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 (ca 250 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.

Analytical methods and equipment

The analytical methods used have been described elsewhere [8]. 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°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 Philips analytical UP 9800 FTIR spectrometer in the range of 4000–400 cm^{-1}.

Results and discussion

As reported by some authors [5, 6] derivative curves obtained for desorption of pyridine from Ni^{2+}-exchanged montmorillonite exhibit strong maxima at ca 40, 90, and 360°C, the latter having been attributed to desorption of base from Brönsted acid sites. However, IR spectra of pyridine adsorbed on Ni^{2+}-exchanged montmorillonite were dominated by intense bands at ca 1450 and 1607 cm^{-1} which are diagnostic of Lewis-bound pyridine [6]. From this aspect, using TG, DTG and IR spectra, we have also directed our attention to the investigation whether 4-methyl- and 4-ethylpyridine occupy in Ni^{2+}-exchanged montmorillonite predominantly Lewis or Brönsted acid sites.

Stoichiometry of thermal decomposition

TG and DTG curves of Ni^{2+}-exchanged montmorillonite (I) and intercalation products pyridine/Ni-MMT (II), 4-methylpyridine/Ni-MMT (III), and 4-ethylpyridine/Ni-MMT (IV) are shown in Figs 1–4. 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 curve at ca 82°C (Table 1) while the second one is connected with a release of water molecules from hydroxide groups (temperatures for maxima of peaks, T_p, on DTG curve at about 656°C). The py, 4-Mepy, and 4-Etpy exchanged montmorillonite (samples II–IV, Figs 2–4) exhibit three desorption peaks with maxima in the regions of 46–84, 342–420 and 636–650°C, respectively (Table 1). In accordance with Breen [7] the first and second peaks correspond to the release of physisorbed and chemically bonded py, 4-Mepy and 4-Etpy while the third ones may be assigned to lattice dehydroxylation of R-py/Ni^{2+}-MMT.

Table 1 Thermal analysis results for the release of pyridine (py), 4-methylpyridine (4-Mepy) and 4-ethylpyridine (4-Etpy) for Ni^{2+}-exchanged montmorillonites (20–700°C)

No.	Sample	TG: Δm/%			DTG: T_p/°C		
		I	II	III	I	II	III
I	Ni-MMT	16.6	–	5.3	82	–	656
II	py/Ni-MMT	8.3	4.3	3.9	84	367	650
III	4-Mepy/Ni-MMT	5.2	8.7	3.4	46	342 420	644
IV	4-Etpy/Ni-MMT	6.2	11.3	3.1	52	407	636

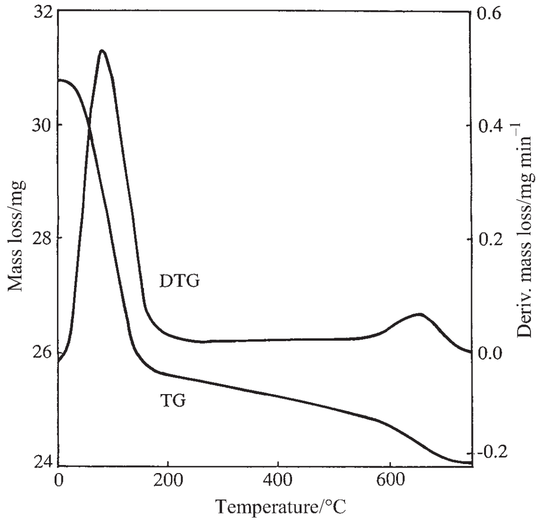

Fig. 1 TG and DTG curves of Ni^{2+}-exchanged montmorillonite. Sample mass: 30.7379 mg

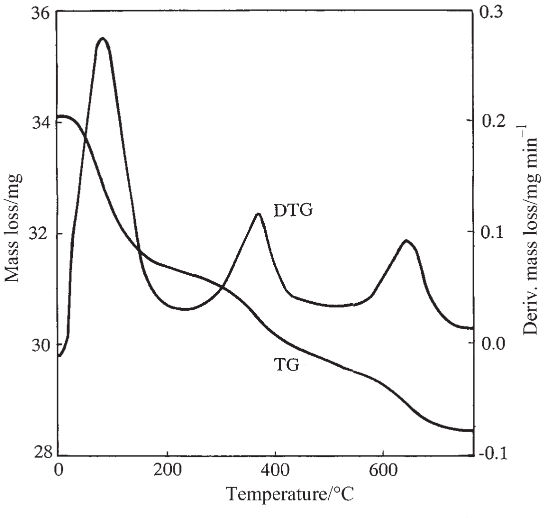

Fig. 2 TG and DTG curves of intercalation product pyridine-Ni^{2+}-exchanged montmorillonite. Sample mass: 34.1298 mg

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

$$py/Ni^{2+}\text{-MMT}<4\text{-Mepy}/Ni^{2+}\text{-MMT}<4\text{-Etpy}/Ni^{2+}\text{-MMT}$$

i. e. the amounts of the adsorbed R-py are increasing with increase of the volume of R-py.

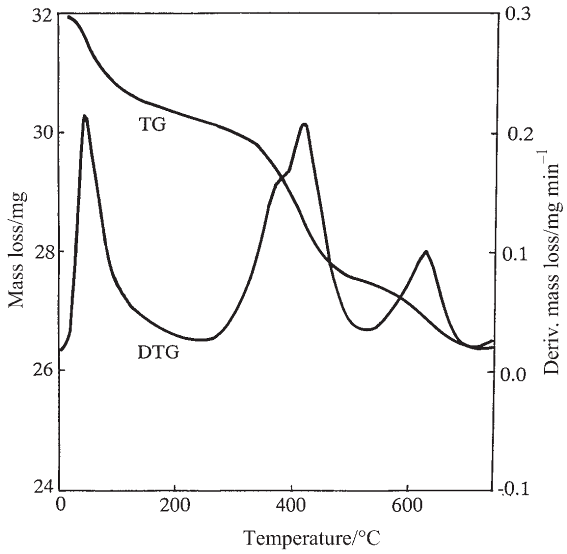

Fig. 3 TG and DTG curves of intercalation product 4-methylpyridine-Ni^{2+}-exchanged montmorillonite. Sample mass: 31.9362 mg

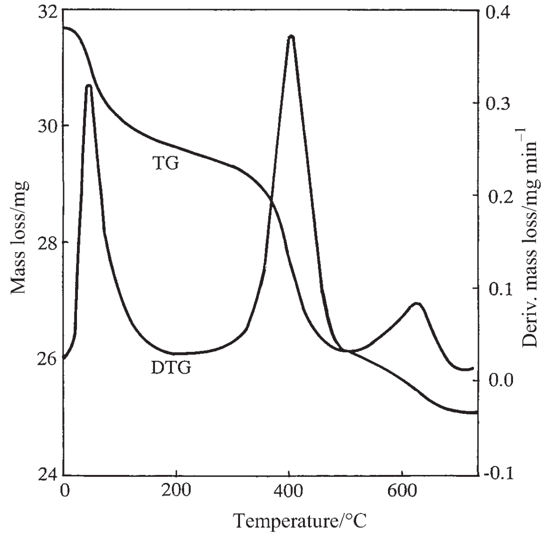

Fig. 4 TG and DTG curves of intercalation product 4-ethylpyridine-Ni^{2+}-exchanged montmorillonite. Sample mass: 31.6639 mg

The preliminary results gained by differential scanning calorimetry [10] have given support to the conclusion that the thermal stability of the studied samples is increasing in the same sequence.

Infrared studies

The samples with adsorbed pyridine exhibited IR absorption bands that were assigned to physisorbed pyridine (1434 and 1485 cm^{-1}), hydrogen-bonded pyridine (753 and 1590 cm^{-1}), Lewis-bound pyridine (1445, 1485, 1578, 1590, and 1613 cm^{-1}) and the pyridinium cation (1485, 1540, 1606, and 1635 cm^{-1}) [9].

Representative IR spectra of the studied samples are presented in Fig. 5. The significant difference between Ni-MMT (I) and adsorption products (II–IV) can be observed in the region 1400–1700 cm^{-1}. Ni-MMT showed one band in the H_2O deformation region at ca 1634 cm^{-1} assigned to 'bound water' [4]. The samples with R-py exhibit in this region a double peak at ca 1640 and 1620 cm^{-1} (sample II at ca 1640, 1630 and 1608 cm^{-1}). On the other hand the adsorption products II–IV showed another peak (Fig. 5). The peaks at 1440–1461, 1491–1510 and 1608–1622 cm^{-1} may be attributed to Lewis bound pyridine. Since the band at 1595 cm^{-1} [11] has not been observed the occurrence of R-pyridine hydrogen-bonded to water in the studied systems is not probable. Moreover, the presence of a peak at ca 1550 cm^{-1} for sample II suggested the presence of some Brönsted bound pyridine in the py/Ni-MMT. However, the major type of acid site in the R-py/Ni^{2+}-exchanged montmorillonite is of electron accepting or Lewis acid character. This is in agreement with literature data. Breen [7] has shown that a prevail feature of IR spectra of py/Ni^{2+}-MMT is the overall dominance of bands associated with Lewis bound pyridine in contrast to the results 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 bands at 1540 cm^{-1}.

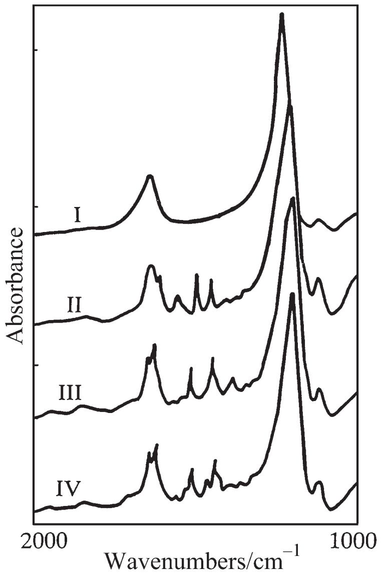

Fig. 5 Infrared spectra of products I–IV in 1000 to 2000 cm^{-1} range

Conclusions

This investigation shows that:

a) The bonds between R-py and Ni^{2+}-exchanged montmorillonite (*R*=H, CH_3, C_2H_5) predominantly exhibit Lewis acid character. This is in a marked contrast to the predominantly Brönsted character shown by trivalent cation-exchanged clays [5].

b) The thermal stability of studied samples and the total amount of the R-py inserted in the porous structure of Ni-*MMT* increase in the following sequence:

$$\text{py/Ni-MMT} < \text{4-Mepy/Ni-MMT} < \text{4-Etpy/Ni-MMT}$$

i. e. the influence of the substituent on the pyridine ring is evident.

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