Journal of Thermal Analysis and Calorimetry, 94 (2008) 1, 69–73

CHARACTERIZATION AND THERMAL PROPERTIES OF Ni-EXCHANGED MONTMORILLONITE WITH BENZIMIDAZOLE

E. Jóna[1]*, M. Sapietová*[1]*, S. Šnircová*[1]*, M. Pajtášová*[1]*, D. Ondrušová*[1]*, V. Pavlík*[1]*,*
L'. Lajdová[1] *and S. C. Mojumdar*[2,3]*

[1]Department of Chemistry and Technolgy of Inorganic Materials, Faculty of Industrial Technologies, University of Trenčín
02032 Púchov, Slovakia
[2]Department of Chemical Engineering and Applied Chemistry, University of Toronto, 200 College St., Toronto, ON, M5S 3E5, Canada
[3]University of New Brunswick, Saint John, NB, E2L 4L5, Canada

Thermal analysis (TG, DTG), powder diffraction analysis (XRD) and infrared (IR) spectra were used to study of composition and release of benzimidazole from Ni(II)-exchanged montmorillonite under heating. Diffraction analysis indicated that benzimidazole molecules are intercalated into the interlayer space of montmorillonite. IR spectra and the analytical characteristics have shown that different type of interactions of benzimidazole is connected with different reaction conditions (acid or neutral solution). The release of benzimidazole from Ni(II)-montmorillonite under heating from studied samples proceeds in three distinct steps. The first step can be assigned to the release of water molecules while the last (third) one corresponds to the lattice dehydroxylation. The second step can be assigned to release of chemically bonded benzimidazole.

Keywords: *benzimidazole, diffraction, Ni-exchanged montmorillonite, spectral properties, thermal*

Introduction

Systematic thermoanalytical research on the most common dioctahedral smectite, montmorillonite, started with the well-known work of Le Chatelier [1], which demonstrated that, when this clay mineral is heated, the first stage involves the endothermic release of water molecules adsorbed on the outer and the inner surfaces. In the second stage a further endothermic effect occurs, which is related to the release of water from hydroxide groups in the octahedral layer of three-layered structure. The first endothermic effect is usually attributed to dehydration and the second to dehydroxylation [2].

During the last decades much interest was devoted to the interactions between montmorillonite and heterocyclic organic compound with the purpose of determining the thermal stability and structure of the organo-clay complexes [3, 4]. Since the clay surface and its interlayer space are populated by Brönsted and Lewis acids and basic sites, the principal interactions between the clay and the adsorbed organic compounds are of the acid-base type [5]. Some methods such as thermal analysis (TG, DTG, DTA) and IR spectroscopy, were used to study of desorption of pyridine and pyridine derivatives from Co-, Ni- and Cu-exchanged montmorillonite [6–10]. It was found that release of pyridine derivatives under heating (20–700°C) proceeds in three or four distinct steps. The first step can be assigned to the release of physically sorbed pyridine derivatives while the last one corresponds to the lattice dehydroxylation. The second step and/or second and third steps can be assigned to release of chemically bonded pyridine derivatives in the interlayer space of montmorillonite.

Among numerous organic species the heterocyclic compounds containing one benzene ring in their structure represent important and widely used chemical agents. Unfortunately, many of them exhibit pronounced carcinogenic effects [11] and montmorillonite could be used as one of the suitable hosts exhibiting desirable properties. However, benzimidazole acts as a ligand in a variety of biological molecules [12] and is used in model compounds for metaloproteins [13]. It is known [14] that the coordination ability of benzimidazole is strongly dependent on the pH of reaction solution in near-neutral and alkali environments. Unprotonated benzimidazole is coordinated to the control atom via the unshared electron pair of nitrogen. In sufficiently acid media both electron pair of nitrogen are occupied (BIH^+) and benzimidazole (BI) does not act as a ligand.

There has been considerable interest among researchers [15–52] in the study of organic-inorganic compounds/materials including their thermal, spectral, X-ray, microscopic, intercalation, biological and

---

* Author for correspondence: scmojumdar@hotmail.com

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

ion-exchange properties. In this paper TG, DTG, XRD and IR spectra have been used to study and the release of benzimidazole from Ni-exchanged montmorillonite under heating.

Experimental

Materials

Less than 2 μm of Jelšový Potok bentonite was prepared from a bulk sample and converted into the monoionic Ca-form using standard methods [7]. The structural formula as calculated from the chemical analysis of the fine fraction is as follows:

$$Ca_{0.48}(Si_{7.59}Al_{0.41})(Al_{3.06}Fe_{0.34}Mg_{0.63})(OH)_4O_{20}$$

The cation exchange capacity (CEC), determined according to the method [53] was 0.96 mmol Me^+ g^{-1}.

The Ni(II)-exchanged montmorillonite was prepared from the Ca-form (3 g) by addition of a $NiCl_2$ solution (450 cm^{-3}, c=1 mol dm^{-3}) and the mixture was stirred shortly 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^- ions and finally dried at 60°C. The interlayer Ni(II) in Ni(II)-montmorillonite was 0.41 mmol Ni(II) g^{-1}.

The reaction of benzimidazole with Ni(II)-montmorillonite was performed by suspending 1 g of Ni(II)–MMT in 100 cm^3 of aqueous solution of benzimidazole with a concentration of 0.02 mol dm^{-3}. The appropriate pH value was adjusted with aqueous solution of HCl or NaOH. The suspensions were stirred at room temperature for 48 h. The solids were separated from the solution by filtering, washed with 200 cm^3 of water and dried at 50°C. The amount of Ni(II), which was released from Ni(II)–montmorillonite in reaction with benzimidazole, was determined by complexometric titration.

Methods

The thermal properties were studied with a TA Instrument SDT 2960. The measurements were carried out in nitrogen using a platinum crucible. A sample mass of 20–25 mg and heating rate 10°C min^{-1} were used. The X-ray diffraction profiles of pressed powder samples were recorded on a Philips PW 1050 X-ray diffractometer in the range 4–400 2Θ using CuK_α radiation. Infrared spectra were measured in KBr pellets on a Nicolet 750 magna spectrometer in the 450–4000 cm^{-1} range.

Results and discussion

Preparation and diffraction properties of studied samples

The starting material for the preparation of intercalated compounds was montmorillonite in its Ca-form. In the process of ion exchange, a montmorillonite with a Ni(II) content of 0.41 mmol g^{-1} was synthesized. This corresponds to nearly full exchange capacity of the clay. The formation of a Ni(II) aqua complex in the interlayer space of the clay is connected with interlayer distance 1.44 nm (Table 1).

When the reaction of Ni(II)-exchanged montmorillonite with benzimidazole solution was performed in acid medium (pH=2), an ionic exchange of Ni(II) for benzimidazolium ion BIH^+ took place (Fig. 1). This is proved by analysis that this sample contains no Ni(II) ions (sample BI-1, Table 1). The interlayer distance of the montmorillonite decreases to 1.37 nm (Table 1) which indicates a flat monolayer structure of the interlayer compound.

The reaction of benzimidazole with Ni(II)–montmorillonite, which was performed in nearly neutral solution (pH=7.84), lead to the formation of the complex with a molar ratio of Ni(II): benzimidazole=1:2 (sample BI-2, Table 1) (this sample is slightly green). The coordination sphere of this complex probably obtain still two water molecules and two silicate oxygen atoms, as in the case of Cu(II)-montmorillonite [14]. The d_{001} value is shifted to 1.56 nm (Table 1).

Table 1 The pH values of benzimidazole reaction solutions, the amount of adsorbed benzimidazole (BI_{ads}), the number of related Ni(II) ions ($Ni(II)_{rel}$) and montmorillonite interlayer space (d_{001})

Sample	pH	BI_{ads}/ mmol g^{-1}	$r(Ni(II)_{rel})$/ mmol g^{-1}	d_{001}/ nm
Ni-MMT	–	–	–	1.44
BI-1	2.00	0.84	0.41	1.37
BI-2	7.84	0.89	0	1.56

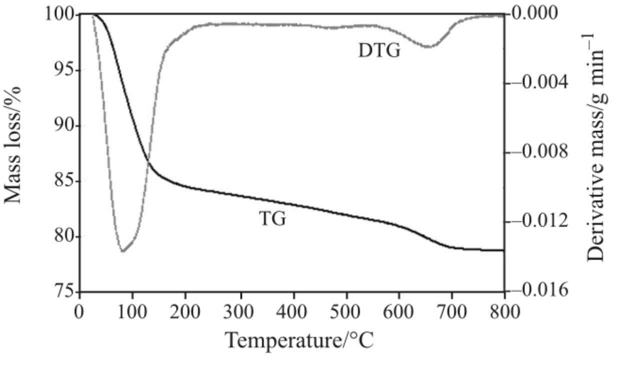


Fig. 1 TG and DTG curves of Ni–MMT Heting rate 10°C min^{-1}

Table 2 The some IR wavenumbers (3200–1300 cm^{-1}) of benzimidazole (BI), benzimidazolium chloride (BIHCl) and studied samples with benzimidazole (BI-1, BI-2)

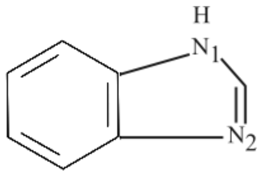
BI	BI HCl	BI-1	BI-2	Assignment
–	3150sh	3148w	3153vw	$\upsilon_{(NH)}$
3113w	3129m	3128sh	3120sh	$\upsilon_{(CH)}$
1620m	1619s	1626m	1626m	$\upsilon_{(CC)}$
1588m	1577w	–	1596w	$\delta_{(NH)inp.}$
–	1531s	1537w	–	$\delta_{(NH)inp.}$
1495m	1499w	1500w	1518s	$\upsilon_{(CC)}$
1478s	–	–	1500vs	$\upsilon_{(CC)}$
1459s	1449vs	1451vs	1463w	$\upsilon_{(CC)}$
–	1393vs	1389w	–	$\upsilon_{(CH)}$
1363s	–	–	1356sh	$\upsilon_{(CH)}$
1301s	–	1308w	1308w	$\upsilon_{(CH)}$

IR spectral properties of studied samples

The IR spectra of the samples BI-1 and BI-2 show bands characteristic of heterocyclic nitrogen compounds. However, the number, positions and relative intensities of the band depend upon the type of interlayer complex (Table 2).

The IR spectrum obtained from benzimidazolium montmorillonite (sample BI-1) shows in studied region band of NH groups at 3148 cm^{-1}. The band at 1537 cm^{-1}, which is typical of benzimidazolium chloride and other benzimidazolium salts [54], can also be observed. This band may be regarded as the bending mode of the NH groups of the protonated benzimidazole ring. The bands of the CC and CN stretching vibrations of the benzimidazolium cation in the range 1300–1500 cm^{-1} are remarkably reduced in intensity, which indicates a strong intercalation of the organic molecule with the environment.

The IR spectrum of sample BI-2 illustrate that the benzimidazole ligand vibrations are shifted from those of the free ligand. The presence of NH-stretching and NH-bending mode peaks indicates that the ligand proton remains bound on the nitrogen atom (at the N_1 position) on the benzimidazole. Thus, the Ni to neutral benzimidazole ligand bonding takes place through the further nitrogen atom (at the N_2 position):



Thermal properties of studied samples

TG and DTG curves of Ni(II)-exchanged montmorillonite (Ni-MMT) and intercalation products with benzimidazole (BI-1, BI-2) are shown in Figs 1–3. The thermal decomposition of Ni-MMT 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 98°C (Table 3) while the second one is connected with a release of water molecules from hydroxide groups (temperature of peak maxima, T_p, on the DTG curve at about 650°C) [7]. The benzimidazole exchanged montmorillonite (samples BI-1 and BI-2), Figs 2 and 3) exhibit three desorption peaks with maxima of peaks on the DTG curve at ca 60–62, 427–450 and 600–625°C (Table 1). In accordance with Luptáková

Table 3 Thermal analysis results of studied samples: Ni–MMT, BI-1 and BI-2

Sample	TG: Δm/%			DTG: T_p/°C		
	Steps: I.	II.	III.	I.	II.	III.
Ni-MMT	18.8	–	5.0	98	–	650
BI-1	7.5	10.2	3.3	60	450	625
BI-2	5.6	10.0	3.2	62	427	600

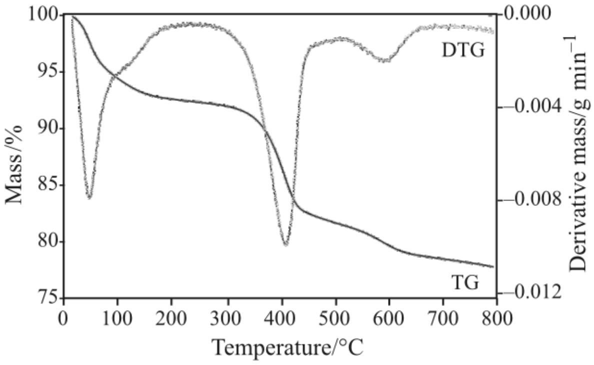


Fig. 2 TG and DTG curves of BI-1 (BIH$^+$/Ni–MMT) heating rate 10°C min^{-1}

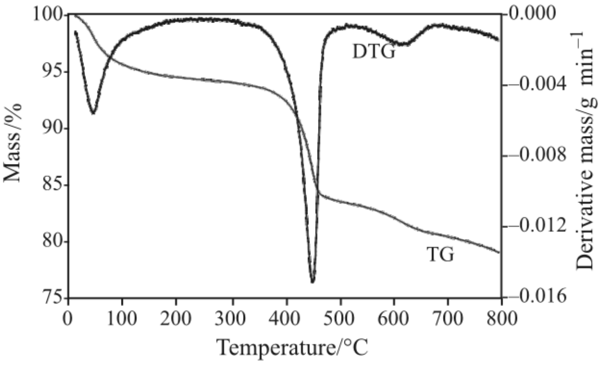


Fig. 3 TG and DTG curves of BI-2 (BI/Ni–MMT)

and Plesch [14], the thermal decomposition of the samples with benzimidazole begins in all cases with a process of water release which is complete by ca 250°C (Figs 2 and 3). The second step on TG curve is connected with endothermic release of benzimidazole (in nitrogen atmosphere) because the typical NH and CC vibration of benzimidazole in IR spectra at 500°C are disappeared. The third step may be assigned to lattice dehydroxylation.

Conclusions

The presented results revealed that Ni(II)-exchanged montmorillonite has provided suitable reaction medium for the incorporation of organic base (benzimidazole) in its porous structure.

The changes in the powder diffraction patterns of the intercalation species in comparison with Ni(II)–montmorillonite indicate the presence of benzimidazole in the interlayer space. The formation of different type of interaction of benzimidazole to Ni(II) in the silicate interlayers is influenced by the reaction conditions. In the nearly neutral conditions benzimidazole is coordinated to Ni(II). In a strongly acid solution, a nearly stoichiometric ionic exchange of benzimidazolium ion for Ni(II) ions takes place.

The thermal effect accompanying the escape of benzimidazole from intercalation products in the temperature interval 20–700°C indicate that the stoichiometry of thermal decomposition (stepwise character) is similar for studied samples with benzimidazole (BI-1 and BI-2). TG and DTG curves exhibit in this region three steps and also the total amounts of the benzimidazole inserted in the porous structure of the studied species are similar.

Acknowledgements

This work has been supported by the fund of the Slovak Grants Agency VEGA No .1/3161/06 Slovak Ministry of Education.

References

1 H. Le Chatelier, Bull. Soc. Fr. Mineral Crystalogr., 10 (1887) 204.
2 V. Š. Fajnor and K. Jesenák, J. Thermal Anal., 46 (1996) 489.
3 D. Malferrari, M. F. Brigatti, A. Laurora, L. Medici and S. Pini, J. Therm. Anal. Cal., 86 (2006) 116.
4 D. Ovadyahu, I. Lapides and S. Yariv, J. Therm. Anal. Cal., 87 (2007) 125.
5 S. Yariv, Thermochim. Acta, 274 (1996) 1.
6 C. Breen, Clay Miner., 26 (1991) 473.
7 E. Jóna, M. Kubranová, A. Sirota and M. Kopcová, J. Therm. Anal. Cal., 63 (2001) 807.
8 E. Jóna, M. Kubranová, S. C. Mojumdar and M. Kopcová, Chem. Pap., 56 (2002) 295.
9 M. Kubranová, E. Jóna, E. Rudinská, K. Nemčeková, D. Ondrušová and M. Pajtašová, J. Therm. Anal. Cal., 74 (2003) 251.
10 E. Jóna, G. Rudinská, M. Sapietová, V. Pavlík, M. Drábik and C.S. Mojumdar, J. Therm. Anal. Cal., 90 (2007) 687.
11 V. Luptáková and J. Horváth, Chem. Pap., 49 (1995) 110.
12 W. Kaim and B. Schwederski, Bioorganische Chemie. B. G. Teubmer, Stuttgart, Germany 1991.
13 G. Plesch, C. Friebel, S. A. Warda, J. Sivý and O. Švajlenová, Trans. Met. Chem., 22 (2004) 433.
14 V. Luptáková and G. Plesch, Clay Miner., 40 (2005) 292.
15 Y. Sawant, V. M. S. Verenkar and S. C. Mojumdar, J. Therm. Anal. Cal., 90 (2007) 669.
16 S. C. Mojumdar, M. Sain, R. Prasad, L. Sun and J. E. S. Venart, J. Therm. Anal. Cal., 90 (2007) 653.
17 K. G. Varshney, V. Jain, A. Agrawal and S. C. Mojumdar, J. Therm. Anal. Cal., 86 (2006) 609.
18 H. S. Rathore, G. Varshney, S. C. Mojumdar and M. T. Saleh, J. Therm. Anal. Cal., 90 (2007) 681.
19 D. Czakis-Sulikowska, A. Czylkowska and A. Malinowska, J. Therm. Anal. Cal., 67 (2002) 667.
20 S. C. Mojumdar, K. Lebrušková and D. Valigura, Chem. Pap., 57 (2003) 245.
21 K. G. Varshney, A. Agrawal and S. C. Mojumdar, J. Therm. Anal. Cal., 90 (2007) 721.
22 I. Dananaj, J. Frankovska and I. Janotka, Applied Clay Sci., 28 (2005) 223.
23 G. Madhurambal, P. Ramasamy, P. A. Srinivasan and S. C. Mojumdar, J. Therm. Anal. Cal., 90 (2007) 673.
24 S. C. Mojumdar and L. Raki, J. Therm. Anal. Cal., 85 (2006) 99.
25 K. G. Varshney, A. Agrawal and S. C. Mojumdar, J. Therm. Anal. Cal., 90 (2007) 731.
26 S. C. Mojumdar, M. Melník and E. Jóna, J. Anal. Appl. Pyrolysis, 53 (2000) 149.
27 S. C. Mojumdar, K. G. Varshney, P. Gupta and A. Agrawal, Res. J. Chem. Environ., 10 (2006) 85.
28 S. C. Mojumdar, K. G. Varshney and A. Agrawal, Res. J. Chem. Environ., 10 (2006) 89.
29 H. S. Rathore, K. Ishratullah, C. Varshney, G. Varshney and S. C. Mojumdar, J. Therm. Anal. Cal., DOI: 10.1007/s10973-008-9191-z.
30 A. Ramadevi and K. Srinivasan, Res. J. Chem. Environ., 9 (2005) 54.
31 G. Sivakumar, Md. R. Ahmed, S. Parthiban, S. P. Meenakshisundaram and S. C. Mojumdar, J. Therm. Anal. Cal., DOI: 10.1007/s10973-008-9187-8.
32 R. N. Patel and K. B. Pandeya, Synth. React. Inorg. Met.-Org. Chem., 28 (1998) 23.
33 J. S. Skoršepa, K. Györyová and M. Melník, J. Thermal Anal., 44 (1995) 169.
34 D. Ondrušová, E. Jóna and P. Šimon, J. Therm. Anal. Cal., 67 (2002) 147.
35 E. Jóna, E. Rudinska, M. Sapietova, M. Pajtasova and D. Ondrusova, Res. J. Chem. Environ., 10 (2006) 31.
36 S. C. Mojumdar and L. Raki, J. Therm. Anal. Cal., 82 (2005) 89.
37 E. Jóna, M. Hvastijová and J. Kohout, J. Thermal Anal., 41 (1994) 161.

38 D. Czakis-Sulikowska and A. Czylkowska, J. Therm. Anal. Cal., 71 (2003) 395.
39 S. C. Mojumdar, M. Melník and E. Jóna, J. Therm. Anal. Cal., 56 (1999) 533.
40 R. A. Porob, S. Z. Khan, S. C. Mojumdar and V. M. S. Verenkar, J. Therm. Anal. Cal., 86 (2006) 605.
41 S. C. Mojumdar, L. Martiška, D. Valigura and M. Melník, J. Therm. Anal. Cal., 74 (2003) 905.
42 E. A. Ukraintseva, V. A. Logvinenko, D. V. Soldatov and T. A. Chingina, J. Therm. Anal. Cal., 75 (2004) 337.
43 S. C. Mojumdar, M. Melník and E. Jóna, J. Therm. Anal. Cal., 56 (1999) 541.
44 S. C. Mojumdar, L. Raki, N. Mathis, K. Schmidt and S. Lang, J. Therm. Anal. Cal., 85 (2006) 119.
45 S. C. Mojumdar, G. Madhurambal and M. T. Saleh, J. Therm. Anal. Cal., 81 (2005) 205.
46 K. G. Varshney, A. Agrawal and S. C. Mojumdar, J. Therm. Anal. Cal., 81 (2005) 183.
47 E. Jóna, E. Rudinská, M. Sapietová, M. Pajtášová, D. Ondrušová, V. Jorík and S. C. Mojumdar, Res. J. Chem. Environ., 9 (2005) 41.
48 S. C. Mojumdar, J. Miklovic, A. Krutošíková, D. Valigura and J. M. Stewart, J. Therm. Anal. Cal., 81 (2005) 211.
49 S. C. Mojumdar, Res. J. Chem. Environ., 9 (2005) 23.
50 G. Madhurambal, S. C. Mojumdar, S. Hariharan and P. Ramasamy, J. Therm. Anal. Cal., 78 (2004) 125.
51 S. C. Mojumdar, J. Therm. Anal. Cal., 64 (2001) 629.
52 S. C. Mojumdar, K. G. Varshney and A. Agrawal, Res. J. Chem. Environ., 10 (2006) 89.
53 W. H. Hendershot and M. Dugnette, Soil Sci. Soc. Am. J., 50 (1986) 605.
54 B. Borah and J. L.Wood, Can. J. Chem., 50 (1976) 2470.

DOI: 10.1007/s10973-008-9190-0