

## Ni-EXCHANGED MONTMORILLONITE WITH METHYL-, DIMETHYL- AND TRIMETHYLAMINE AND THEIR THERMAL PROPERTIES

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The influence of different steric properties of methylamine (MA), dimethylamine (DIMA) and trimethylamine (TRMA) on the type of interactions with Ni-exchanged montmorillonite and thermal properties of these materials were studied. The results of diffraction, spectral (IR) and thermal (TG, DTG) analysis show that MA, DIMA and TRMA are intercalated into the interlayer space of montmorillonite. Thermal decomposition in the temperature interval 20–450 °C of studied samples with MA and DIMA proceeds in three steps (the release of chemisorbed amines, coordinated amines and alkylammonium cations) while the sample with TRMA decompose only in two steps (the peak corresponds to the release of coordinated TRMA is absent). The effect of different steric properties of individual amines is evident.

**Keywords:** methyl-, dimethyl- and trimethylamines, Ni-exchanged montmorillonite, thermal decomposition

### Introduction

Intercalated compounds of montmorillonite with aliphatic amines are used in many industrial branches, e.g. as thixotropic agents in lacquers and paints, in lubricants, as adsorbents of organic pollutants and in chromatography for separation of organic compounds and isomers, etc. [1, 2]. They are used for their special properties of hydrophobicity, lyophilicity and swelling in the organic liquids [3].

Many papers have been published concerning the study of the interactions of neutral amines and/or the alkylammonium cations with montmorillonite [4–10]. The arrangement of alkyl chains depends on the layer charge and the alkyl chain length [11, 12]. Short-chain alkylammonium cations are arranged into monolayers, long chain cations form bilayers. Pseudo-trilayers of kinked alkyl chains were observed using the highly charged smectites and long chain alkylamines.

Only few papers deal with thermal effects on these materials [13–15] in spite of the importance of their thermal behavior in many industrial applications. TG and DTA studies of organo-clay coupled with other thermal methods have been recently reviewed

[16, 17]. The present paper describes thermal analyses (TG, DTG), diffraction and spectral data of Ni-exchanged montmorillonite with methyl, dimethyl and trimethylamines. The aim of this study was to investigate the effect of different steric effects of these alkylamines on the type of interactions with Ni-montmorillonite and thermal decomposition of studied materials.

### Experimental

#### *Syntheses of the samples*

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 method [18, 19]. The crystallochemical formula of Ca-MMT is as follows:  $\text{Ca}_{0.48}(\text{Si}_{7.59}\text{Al}_{0.41})(\text{Al}_{3.06}\text{Fe}_{0.34}\text{Mg}_{0.63})(\text{OH})_4\text{O}_{20}$ .

The monoionic form of Ni-MMT was prepared from the Ca-MMT in a way that 450 cm<sup>3</sup> of a NiCl<sub>2</sub> solution ( $c=1 \text{ mol dm}^{-3}$ ) were added to 3 g of Co-MMT, the mixture was stirred for a short time and left to stand for 24 h. After decantation NiCl<sub>2</sub> solution was added again to the solid phase, stirred and left to stand as previ-

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ously. This procedure was repeated four times. The solid product was then washed by water in order to remove the Cl<sup>-</sup> anions and finally dried at 60°C. A thin layer (ca. 250 mg) of monoionic form was explored to alkylamine vapours for 72 h at room temperature.

#### Analytical methods and equipments

The analytical methods used have been described elsewhere [20]. The thermal properties (TG, DTG) were studied on a TA Instrument SDT 2960. The measurements were carried out in nitrogen atmosphere using a platinum crucible. A sample mass of 20–25 mg and heating rate 10°C min<sup>-1</sup> were used.

The infrared absorption spectra were recorded on a Nicolet Magna 750 Fourier Transform IR spectrometer in the range of 400–4000 cm<sup>-1</sup>.

The X-ray diffraction profiles for pressed powder samples were recorded on a Philips PW 1050 diffractometer using CuK<sub>α</sub> radiation.

## Results and discussion

#### Diffraction and spectral properties of studied samples

The interlayer distances from the X-ray diffraction patterns and colour of studied samples are summarized in Table 1.

After the interactions with alkylamines, the basal spacings decreased from 1.44 to ca. 1.23–1.28 nm. Since the basal spaces are close for all studied products, we suppose that the arrangement of alkylamines in the interlayer space is similar. The observed changes in the basal spaces indicated that the alkylamines are intercalated into the interlayer spaces of montmorillonite [21, 22].

The decrease of basal spacing may be, however, partly due to the different hydration of montmorillonite. In order to exclude this possibility, the products were heated at 60°C. It was observed that basal spaces of all products did not change during the heat treatment. From these observations, we have concluded

**Table 1** Representative diffraction data and colour of Ni-MMT and intercalation products

Sample	2θ/°	d <sub>001</sub> /nm	Colour
Ni-MMT(I)	7.11	1.44	light green
Ni-MMT+MA(II)	8.33	1.23	dark green
Ni-MMT+DIMA(III)	8.07	1.27	dark green
Ni-MMT+TRMA(IV)	7.99	1.28	dark green

MMT – montmorillonite, MA – methylamine, DIMA – dimethylamine, TRMA – trimethylamine

that the observed decrease in the basal space was due to the intercalation of the alkyl amines into the interlayer space of montmorillonite.

The changes in colour of studied samples suggest the changes in the coordination sphere of the interlayer Ni<sup>2+</sup> cations. Since these cations were surrounded by water molecules at ambient conditions, the decrease in the basal spaces may be due to the intercalation of the alkylamine into the interlayer spaces of montmorillonite.

The various ways in which alkylamines form bonds in the interlayer space of the Ni-montmorillonite can be deduced from IR spectra of the prepared samples. In the studied region (400–4000 cm<sup>-1</sup>) several peaks of Ni-MMT can be observed that were attributed to the stretching vibrations of OH-groups (3632–3624 cm<sup>-1</sup>) and water (3433–3394 cm<sup>-1</sup>), stretching vibrations of Si–O groups (1033–1020 cm<sup>-1</sup>), deformation vibrations of OH-group (950–800 cm<sup>-1</sup>), AlAlOH at 912–910 cm<sup>-1</sup>, AlMgOH 841–839 cm<sup>-1</sup>, deformation vibrations of Al–O–Si groups at 520–516 cm<sup>-1</sup> and Si–O–Si at 457–453 cm<sup>-1</sup>. The significant difference between Ni-MMT and the intercalated products can be observed first of all in the regions 3300–2300, 2500–2350 and 1633–1460 cm<sup>-1</sup> (Table 2).

The IR spectra obtained from samples with alkylamines show the bands of NH<sub>2</sub> groups at 3433–3420 and 1633–1631 cm<sup>-1</sup> (these bands may be overlapped with bands of δ<sub>H–O–H</sub> vibrations); ν<sub>N–H</sub> vibrations are observed at 3302–3219, 2777–2733 and 2467–2432 cm<sup>-1</sup>; bands of C–H groups at 3022–2962 and 1479–1464 cm<sup>-1</sup>. IR spectra indicated (especially bands at 2777–2733 cm<sup>-1</sup> [23]) that alkylamines are intercalated in the interlayer space of montmorillonite. Coordination of alkylamines causes shifts in its absorption bands from the position observed for the

**Table 2** Some IR spectral data of studied samples

Assignment	ν/cm <sup>-1</sup>		
	Ni-MMT+ MA	Ni-MMT+ DIMA	Ni-MMT+ TRMA
ν <sub>NH<sub>2</sub></sub>	3420	3433	3429
ν <sub>N–H</sub>	3302	3250	3219
ν <sub>C–H</sub>	3022	3003	2962
	2756	2777	2733
ν <sub>N–H</sub>	2461	2432	2467
	2347	2343	2357
δ <sub>NH<sub>2</sub></sub> (δ=N <sup>+</sup> )H	1633	1631	1633
	1510	1510	1510
δ <sub>C–N</sub>	1464	1467	1479
γ <sub>N–H</sub>	910	912	912
γ <sub>N–H</sub>	792	794	794

free amines in solution. The bands at  $1510\text{ cm}^{-1}$ , however, are typical of alkylammonium cations [24]. Thus alkylamines in the studied samples are coordinated to  $\text{Ni}^{2+}$  ions and also may exist as alkylammonium cations.

*Thermal properties of studied samples*

TG and DTG curves of Ni-MMT(I) and intercalation products Ni-MMT+MA(II), Ni-MMT+DIMA(III) and Ni-MMT+TRMA(IV) are shown in Figs 1–4. Thermal data from TG and DTG curves of studied samples are summarized in Table 3.

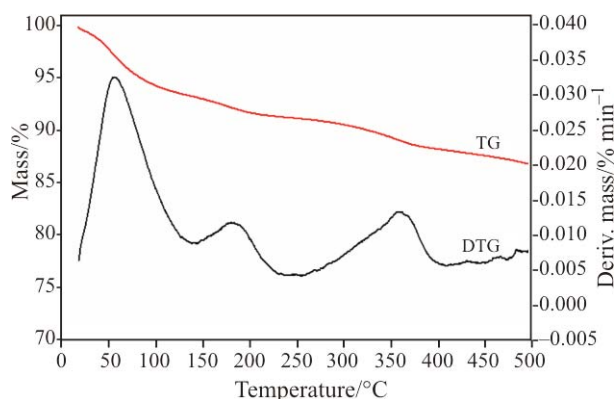
The thermal decomposition of Ni-MMT(I) (Fig. 1) proceeds under dynamic conditions and in the temperature interval 20–450°C in one distinct step. This step can be assigned to the release of adsorbed water molecules with DTG peak at 105°C (Table 3).

The samples Ni-MMT+MA(II) and Ni-MMT+DIMA(III) (Figs 2 and 3) exhibit three desorption peaks on the DTG curves with maxima in the region ~59–61, ~175 and 350–400°C, respectively (Table 3). In accordance with Breen [25] the first peak corresponds to the release of physisorbed  $\text{H}_2\text{O}$  molecules

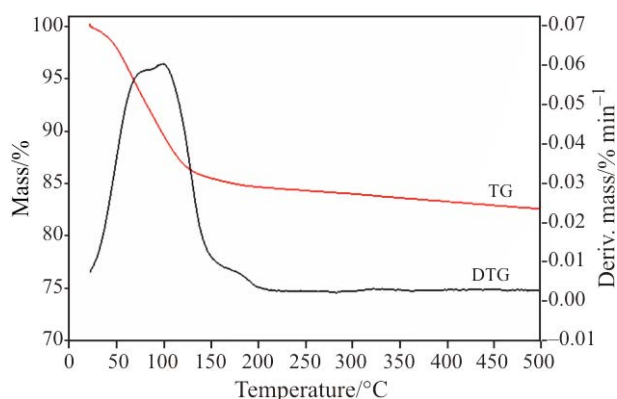
and amines, the second peak corresponds to the coordinated amines while the third one is assigned to protonated amines.

The sample Ni-MMT+TRMA(IV) exhibit only two peaks on the DTG curve (Fig. 4) with maxima at ca. 64 and 380°C.

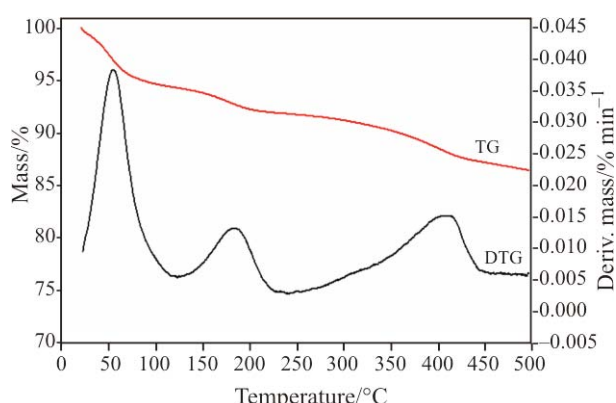
The results suggest that the number of methyl groups in the amines significantly influences the steric effects of ligands and thereby also the complex formation in the silicate interlayers. When the num-



**Fig. 2** TG and DTG curves of Ni-MMT+MA



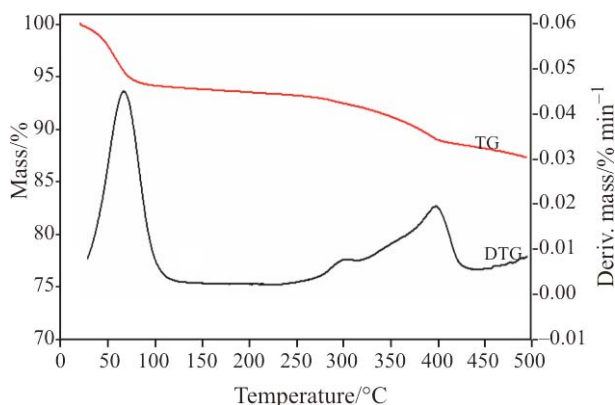
**Fig. 1** TG and DTG curves of Ni-MMT (MMT-montmorillonite)



**Fig. 3** TG and DTG curves of Ni-MMT+DIMA

**Table 3** Thermal analysis results for studied samples in the temperature interval 20–450°C

Sample	TG			DTG
	steps	$\Delta m/\%$	released component	$T_p/^\circ\text{C}$
Ni-MMT(I)	1	15.7	adsorbed $\text{H}_2\text{O}$	105
	1	6.8	adsorbed $\text{H}_2\text{O}+\text{MA}$	61
Ni-MMT+MA(II)	2	2.1	coordinated MA	175
	3	3.3	protonated MA	350
	1	5.7	adsorbed $\text{H}_2\text{O}+\text{DIMA}$	59
Ni-MMT+DIMA(III)	2	2.5	coordinated DIMA	175
	3	4.8	protonated DIMA	400
	1	6.6	adsorbed $\text{H}_2\text{O}+\text{TRMA}$	64
Ni-MMT+TRMA(IV)	2	5.1	protonated TRMA	380



**Fig. 4** TG and DTG curves of Ni-MMT+TRMA

bers of methyl groups are changed (from methylamine to trimethylamine) the possibility of the coordination of the amines is decreased and formation of the protonated amines (the Brönsted interactions) increase. Therefore, trimethylamine gives priority to formation of protonated form (Brönsted interactions), while the methyl- and dimethylamines show as well also Lewis interactions (coordination bonding).

## Conclusions

X-ray powder diffraction, spectral and thermal analysis show that methyl-, dimethyl- and trimethylamines were successfully intercalated into interlayer spaces of nickel(II)-montmorillonite. The presence of coordinated and/or protonated amines in the silicate interlayers is connected with different steric effects of studied amines which also influence the stoichiometry of thermal decomposition of studied materials.

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