

LAYERED SILICATES AND THEIR INTRACATIONS WITH TOXIC ORGANIC COMPOUNDS

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Abstract

The influence of organic compounds: ethylenediamine (EDA), trimethylethylenediamine (TrMeEDA) and tetramethylethylenediamine (TeMe EDA) on the type of interactions with Ni- exchanged montmorillonite were studied. The results of thermal, diffraction and spectral analysis shown that studied diamines are intercalated into the interlayer space of montmorillonite. It was found that EDA is coordinated to Ni²⁺ and alkyldiamines are in protonated forms. The effect of different steric properties of individual diamines is evident.

Keywords: Ni - exchanged montmorillonite, interactions with ethylenediamine and its methyl derivatives

1 Introduction

Much interest was devoted to the interactions between layered silicates and organic compounds (as amines) with the purpose of determining the structure and stability of organic silicate complexes and the type of bonds between silicate components and the adsorbed organic species.

One of the characteristic features of layered silicates (especially montmorillonites) is their structure. The layers are formed by two tetrahedral sheets linked with an octahedral sheet. Isomorphous substitution in the octahedron and /or tetrahedron generates a negative charge on the layers, which is balanced by hydrated exchangeable cations in the interlayer, mostly Ca²⁺, Mg²⁺, Na⁺ in natural samples (but also Ni²⁺, Co²⁺ or Cu²⁺ ions). Organic molecules (as amines) can replace the water which normally occupies the interlayer spaces in the montmorillonite [1].

Many papers have been published concerning the study of the interactions of neutral amines and diamines with montmorillonite [2-4]. The arrangement of alkyl chains depends on the layer charge and the alkyl chain length [5]. Organomontmorillonites with amines are used in many industrial branches, e.g. as tixotropic agents in lacquers and paints, in lubricants, as adsorbents of organic compounds [6]. Montmorillonites are also important in areas of environmental concern, and for such applications a precise knowledge of the interaction mechanisms between different components in the interlayer space of montmorillonite is greatly desirable.

The present paper describes thermal analysis (TG, DTG), diffraction and spectral (IR) data of Ni-exchanged montmorillonite (Ni-MMT) with ethylenediamine (EDA), trimethyl-ethylenediamine (TrMeEDA) and tetramethyl-ethylenediamine (TeMeEDA). The aim of this paper is to investigate the effect of different properties of these diamines on the type of interactions with Ni-montmorillonite and physical properties of prepared samples

2 Experimental

Syntheses of the samples

Less than 2µm 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 method [7,8]. The crystallochemical formula of Ca-MMT is as follows: Ca_{0,48}(Si_{7,59}Al_{0,41})(Al_{3,06}Fe_{0,34}Mg_{0,63})(OH)₄O₂₀.

The monoionic form of Ni-MMT was prepared from the Ca-MMT in a way that 450cm³ of a NiCl₂ solution (c = 1 mol. dm⁻³) were added to 3g of Ca-MMT, the mixture was stirred for a short time and left to stand for 24 h. After decantation NiCl₂ 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 alkylamine vapours for 72 h at room temperature.

Analytical methods and equipments

The thermal properties (TG, DTG) were studied with 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⁻¹ were used.

The infrared absorption spectra were measured I KBr on a Nicolet Magna 750 Fourier Transform IR spectrometer in the range of 400-4000 cm^{-1} .

The X-ray diffraction profiles for pressed powder samples were recorded on a Philips PW 1050 diffractometer using CuK_α radiation.

3 Results and discussion

As reported previously [7,8], IR spectra combined with diffraction (RTG) data and thermal analysis (TG, DTG) can provide a precious information about the character of bonds between the adsorbed diamines and monoionic form of montmorillonite (Ni-MMT).

Diffraction properties and colour of studied samples

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

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

Sample	$2\Theta/^\circ$	d_{001} / nm	Colour
Ni-MMT (I.)	7,06	1,45	Grey
Ni-MMT EDA (II.)	7,56	1,36	Rose-grey
Ni-MMT TrMeEDA (III.)	7,38	1,39	Yellow-grey
Ni-MMT + TeMeEDA (III.)	7,55	1,36	White

After the interactions of diamines with montmorillonite, the basal spacings decreased from 1,45 nm to 1,36 - 1,39 nm and are close for all studied product. We assume that:

- the arrangement of diamines in the interlayer space is similar;
- the observed changes in the basal spacing are connected with the intercalation of diamines into the interlayer spaces of montmorillonite [9-11].

The changes in colour of studied samples suggest the changes in the coordination sphere of the interlayer Ni^{2+} cations. Since these cations were surrounded by water molecules at ambient conditions, the decrease in the basal spacing may be due to the intercalation of the diamines into the interlayer spaces of montmorillonite.

Spectral properties of studied samples

The various ways in which diamines form bounds in the interlayer space of montmorillonite can be deduced from infrared (IR) spectra. In the studied region (400 – 4000 cm^{-1}) several peaks of Ni-MMT can be observed that were attributed to the stretching vibrations of OH-groups (3618 - 3620 cm^{-1}) and water (3383 cm^{-1}), stretching vibrations of Si-O groups (1020 - 1105 cm^{-1}), deformation vibrations of OH-groups (835 – 912 cm^{-1}), AlAlOH (910 – 914 cm^{-1}), AlMgOH (835 - 839 cm^{-1}), deformation vibrations of Al-O-Si groups (516 – 518 cm^{-1}) and Si-O-Si (459 – 462 cm^{-1}) [10-11].

The significant differences between Ni-MMT and the intercalated products can be observed first of all in the region 1400 – 1700 cm^{-1} (Table 2).

Table 2 Characteristic IR spectral data of Ni-MMT with EDA, TrMeEDA and TeMeEDA

Assignment	ν / cm^{-1}			
	Ni-MMT (I)	I+EDA	I+TrMeEDA	I+TeMeEDA
$\nu(\text{NH}_2)$	-	3356,3283	-	-
$\nu(\text{NH}_2)^+$	-	-	3439	-
$\nu(\text{NH})^+$	-	-	-	3435,3300
$\nu(\text{CH})$	-	2941,2883	2953,2870	2953,2866
$\delta(\text{H-O-H})$	1633	-	-	-
$\nu(\text{NH}_2)^+$	-	-	1631	-
$\nu(\text{NH})^+$	-	-	-	1630
$\delta(\text{NH}_2)$	-	1585	-	-

Whereas Ni-MMT+EDA shows in this region one peak at 1585 cm^{-1} assigned to the deformation vibrations of NH_2 groups, Ni-MMT+TrMeEDA and Ni-MMT+TeMeEDA exhibit in this region peak at ~ 1631 cm^{-1} . It is known, that coordination of EDA causes shift of peak at ~ 1630 cm^{-1} . The NH_2 scissoring vibration at ~ 1626 cm^{-1} in solution, is displaced to ~ 1590 cm^{-1} on coordination [3,6].

Thus EDA is coordinated to Ni^{2+} and TrMeEDA and TeMeEDA occur in studied samples in protonated form. These result suggest than when the numbers of methyl groups are changed (from EDA to tetramethyl EDA) the possibility of the coordination of the diamines is decreased and formation of protonated diamines increase.

Thermal properties of studied samples

Thermal analysis results are summarized in Table 3 and typical DTG curves of studied samples are shown in Figure 1.

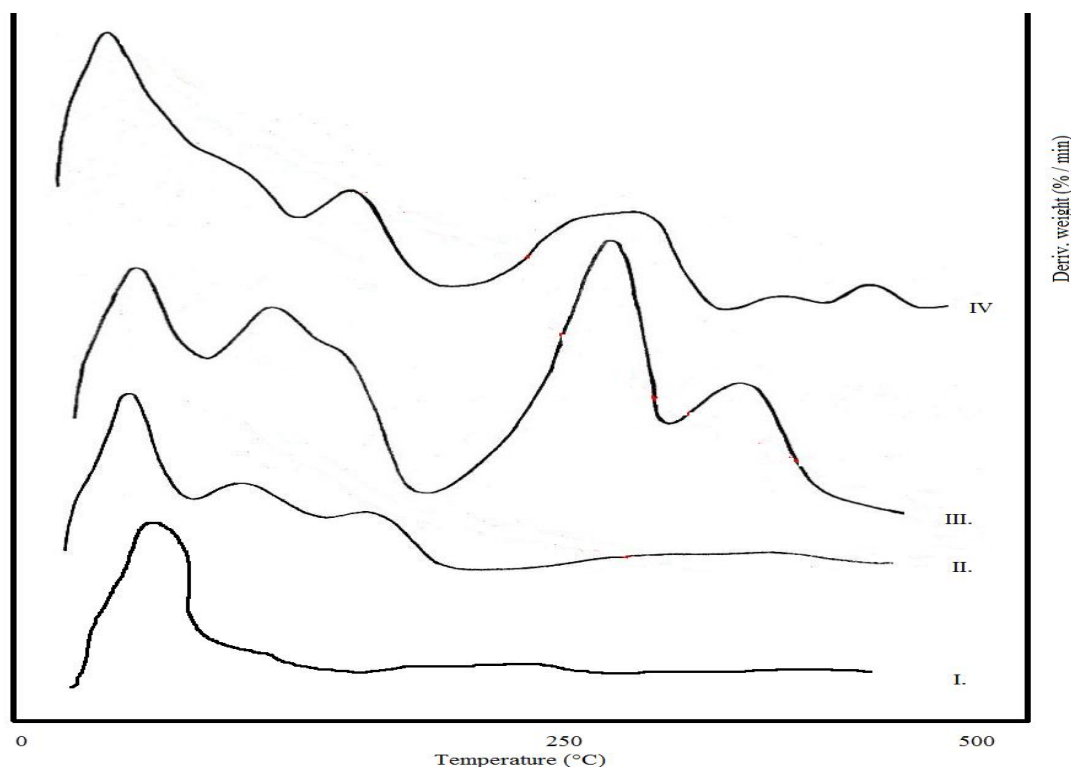


Fig.1 DTG curves of Ni-MMT (I), Ni-MMT + EDA (II), Ni-MMT + TrMeEDA (III), Ni-MMT + TeMeEDA (IV)

Table 3 Results of Thermal analysis for studied samples in the temperature interval 20 – 550°C

Sample	TG Step	TG $\Delta m / \%$	DTG $T_p / ^\circ\text{C}$	Released components and processes
Ni-MMT (I)	1	14,9	90	Water molecules
	2	0,7	180	Dehydroxylation
Ni-MMT + EDA (II)	1	4,3	66	Adsorbed EDA
	2	2,7	133	Coordinated EDA
	3	6,1	450	Dehydroxylation
Ni-MMT + TrMeEDA (III)	1	3,6	67	Adsorbed TrMeEDA
	2	4,7	150	Coordinated TrMeEDA
	3	5,2	351	Protonated TrMeEDA
	4	5,6	427	Dehydroxylation
Co-MMT + TeMeEDA (IV)	1	8,2	58	Adsorbed TeMeEDA
	2	3,2	149	Coordinated TeMeEDA
	3	5,0	337	Protonated TeMeEDA
	4	3,1	480	Dehydroxylation

The thermal decomposition of Ni-MMT proceeds under dynamic conditions in the temperature interval 20 - 500 °C in two distinct steps (Tab.3). The first step can be assigned to the release of water molecules with DTG peak at ~ 90°C while the second one is connected with a release of water molecules from hydroxylgroups of Ni-MMT (lattice dehydroxylation). Three steps of decomposition of Ni-MMT+EDA (II) are observed in the

temperature interval under study. The first step can be assigned to the physically adsorbed water molecules and EDA while the second peak can be assigned to the coordinated EDA and third one to the dehydroxylation (Fig.1). The thermal decomposition of Ni-MMT + TrMeEDA (III) and Ni-MMT + TeMeEDA (IV) proceeds in for steps. The first step can be assigned to the release of adsorbed water and diamine molecules, the second and third steps to the coordinated and protonated diamines while the last one corresponds to the lattice dehydroxylation [3 - 6].

4 Conclusions

X-ray powder diffraction, IR spectra and thermal data show that ethylenediamine (EDA), trimethylethylenediamine (TrMeEDA) and tetramethylethylenediamine (TeMeEDA) were successfully intercalated into interlayer space of Ni (II) – montmorillonite. The presence of coordinated and/or protonated diamines in the silicate interlayers is connected with different steric effects of studied samples.

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