DEHYDRATION AND DEHYDROXYLATION OF REDUCED CHARGE MONTMORILLONITE

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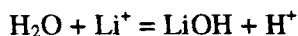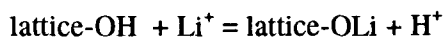
Abstract

Reduced charge montmorillonites (RCM) were prepared by the thermal treatment of lithium-saturated montmorillonite. Samples prepared by mild thermal treatment with lithium contained more water sorbed than the original montmorrilonite. When RCMs were prepared, part of the lithium cations reacted with hydroxyl groups in the octahedral sheet and released protons, which reacted with the structure. Acid treatment probably enhanced the surface area. which was reflected in the amount of water sorbed. Deprotonation of hydroxyl groups was proved by the measurements of the ignition loss. The heating of lithium saturated montmorillonite at higher temperatures brought about the collapse of the interlayers and a decrease in the amount of water sorbed.

Keywords: lithium thermal treatment, dehydration, dehydroxylation, montmorillonite

Introduction

The clay mineral montmorillonite is a member of the group of dioctahedral smectites. Its layers are negatively charged due to the replacement of Al^{3+} by Mg^{2+} in the octahedral sheet and partially to the replacement of Si^{4+} by Al^{3+} in the tetrahedral sheet. The net charge is compensated by exchangeable cations in the interlayer spaces. When montmorillonite containing small exchangeable cations such as Li^+ is heated at about 200°C, these cations migrate into the layers towards the negative centres in the octahedral sheet [1]. Such cations become fixed and unchangeable, and the result of this phenomenon is the reduction of cation exchange capacity (CEC). A few possibilities have been considered for the final location of fixed cations:

- bottom of the pseudohexagonal cavities [2, 3]
- vacant octahedral sites [1, 4, 5]
- part of the cations deprotonate hydroxyl groups or react with residual water molecules [6-8]:

$$\text{lattice-OH} + \text{Li}^+ = \text{lattice-OLi} + \text{H}^+$$

$$\text{H}_2\text{O} + \text{Li}^+ = \text{LiOH} + \text{H}^+$$

– part of the cations remain fixed in the collapsed interlayers [5].

This phenomenon has been used for the preparation of reduced charge montmorillonites (RCM) and some of their properties have been described [9-11].

The RCM samples used in this work were prepared by thermal treatment of lithium saturated montmorillonite at different temperatures. The samples should differ in water content (due to collapsed interlayers) and in the amount of hydroxyl groups due to the proposed deprotonation. The aim of this work was to investigate the dehydration and dehydroxylation of RCM samples.

Experimental

Montmorillonite (M1) was isolated as the <2μm fraction by sedimentation of a 4 % water suspension of Jelsovy Potok bentonite (Central Slovakia). The Li saturated form was prepared by treatment with lithium chloride solution. Li saturated montmorillonite was allowed to dry in air and then crushed to a powder. RCM samples (M2-M8) were prepared by thermal treatment of lithium-saturated montmorillonite. The time of heating was 24 h and the temperatures are listed in Table 1. Samples M1-M8 were saturated with calcium chloride to prepare calcium loaded forms.

Table 1 Temperatures used in the preparation of samples with reduced charge on layers

Sample	$T/^\circ C$
M1	–
M2	105
M3	110
M4	120
M5	130
M6	135
M7	160
M8	210

Thermoanalytical measurements were carried out using a Derivatograph Q-1500 D (MOM, Budapest) at a heating rate of 2 deg.min^{-1}. Before measurements the samples were held in constant humidity atmosphere over a saturated solution of magnesium nitrate for 24 h.

Table 2 Results of chemical analysis (in % of the dry samples) and CEC values (in meq.g^{-1}) of the samples

Sample	M1	M2	M3	M4	M5	M6	M7	M8
SiO$_2$	60.96	61.41	60.78	61.76	62.50	62.60	63.52	63.98
Al$_2$O$_3$	19.24	19.71	19.47	19.97	20.02	20.20	20.39	20.48
Fe$_2$O$_3$	2.40	2.11	2.19	2.17	2.40	2.34	2.36	2.39
TiO$_2$	0.13	0.13	0.13	0.12	0.13	0.11	0.11	0.11
P$_2$O$_5$	0.03	0.10	0.08	0.10	0.07	0.08	0.03	0.09
FeO	0.07	0.07	0.07	0.08	0.08	0.07	0.07	0.07
MnO	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
CaO	3.47	3.33	3.62	2.77	2.37	2.08	1.12	0.54
MgO	4.08	4.38	4.39	4.42	4.43	4.53	4.56	4.71
K$_2$O	0.08	0.04	0.04	0.04	0.06	0.07	0.06	0.07
Na$_2$O	0.06	0.01	0.01	0.03	0.07	0.05	0.13	0.07
Li$_2$O	0.00	0.17	0.20	0.39	0.52	0.65	1.08	1.35
CEC	0.83	0.71	0.65	0.60	0.50	0.46	0.26	0.14

Results and discussion

CEC values and chemical analysis results of the samples are summarized in Table 2. The CEC values of the samples are in the range 0.14-0.83 meq.g^{-1}. The amount of fixed lithium increases from sample M2 to sample M8 and exchangeable calcium decreases from sample M1 to sample M8.

The DTA curves exhibit two peaks. The temperatures of the peaks are given in Table 3. The first peak is strongly endothermic which corresponds to the loss of the sorbed water molecules. The first peaks of samples M1-M4 are distinguished as a double peak with a shoulder at higher temperature. The release of water at the external surface and interlamellar water not bonded to exchangeable cations proceeds at lower temperatures. Water coordinated to calcium ions in the interlayers is bonded more strongly and thus it is liberated at higher temperature. Moreover, after partial dehydration the last molecules of water around the calcium cations become acidic and the following reaction proceeds [11]:

$$Ca(H_2O)^{2+} = Ca(OH)^+ + H^+$$
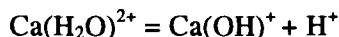
With decreasing amount of calcium cations in the interlayers, the shoulder observed at higher temperature disappeared (samples M5–M8).

Table 3 Dehydration (T_2) and dehydroxylation (T_2) temperatures

Sample	$T_1/^{\circ}C$		$T_2/^{\circ}C$
M1	130	(185)	680
M2	130	(190)	680
M3	135	(190)	670
M4	125	(180)	670
M5	125		680
M6	125		675
M7	120		680
M8	110		685

The temperature of the main dehydration peak is about 130°C for highly charged samples (M1-M6) and it decreases to 110°C for the least charged sample M8. The decrease of layer charge leads to the collapse of interlayers in samples M7 and M8. The collapsed interlayers are non-swelling and water is sorbed on the external surface. External water is bonded less strongly than interlayer water held around the cations, and it is liberated at lower temperature.

The second endothermal peak corresponds to the dehydroxylation of the silicate lattice. This peak occurs at about 680°C and this temperature seems to be independent of the layer charge.

The dependence of water loss on the CEC is demonstrated in Fig.1. The amounts measured by thermal analysis were compared with losses determined by drying, carried out with samples treated in lower humidity atmosphere. Both amounts are referred to 1g of dried sample. The large decrease of CEC causes a reduction in the amount of sorbed water due to the presence of non-expanding interlayers.
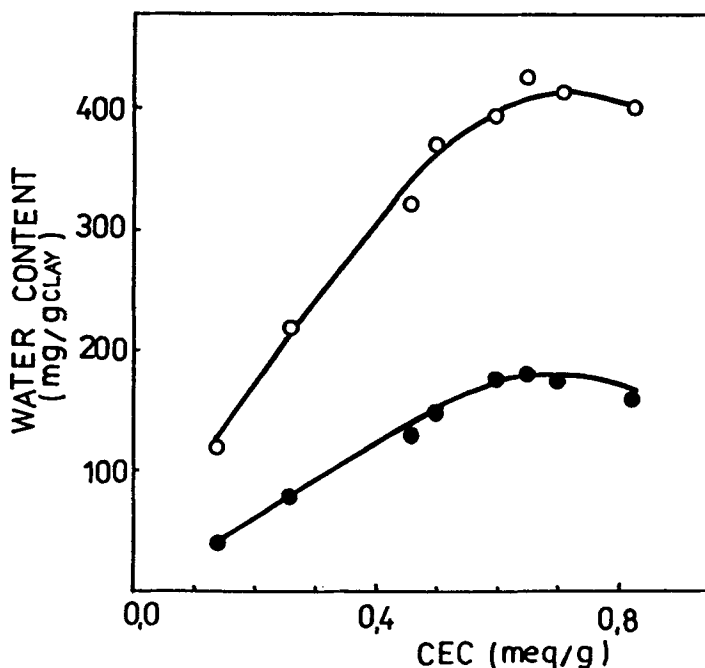

Fig.1 Dependence of loss on drying (•) and amount of sorbed water in samples determinated by thermogravimetry (o) on CEC

Collapsed interlayer spaces did not arise after mild thermal treatment with lithium (samples M1-M4) and no change in water content was expected. However, water contents are slightly higher in samples M2-M4 than in M1, which was confirmed by a detailed study of water sorption on these samples [12]. Migration of lithium cations probably causes an increase in surface area. These are two hypotheses to explain this:

– expansion of the structure, which is provoked by the formation of local trioctahedral structures, can give rise to structural defects at high temperatures

– lithium cations react with hydroxyl groups to release H^+ cations which are very reactive and break down the structure.
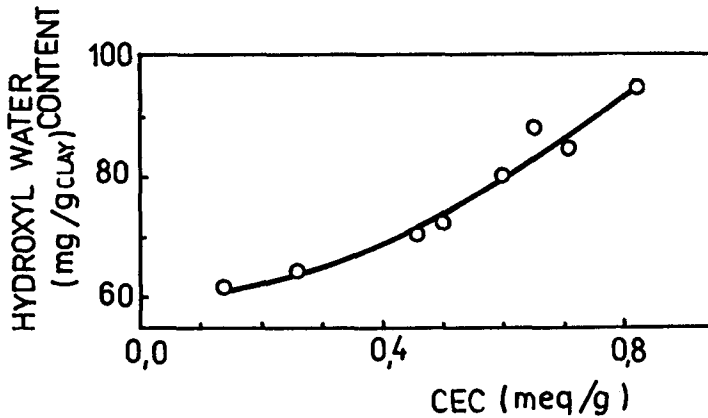

Fig.2 Dependence of the ignition loss (hydroxyl water content) on CEC

Figure 2 shows the dependence of ignition loss and hydroxyl water content on CEC. The amount of hydroxyl groups is lower in RCM samples and it decreases with decreasing CEC. This suggests that part of the lithium cations react with hydroxyl groups to release H^+ cations. These may react with the structure and bring about an increase in the specific surface area as was described above. This was observed after the migration of lithium cations into the layers, until formation of collapsed interlayers commenced. which had the opposite effect.

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Zusammenfassung — Montmorillonite mit reduzierter Ladung (RCM) werden durch eine thermische Behandlung von lithiumgesättigten Montmorilloniten dargestellt. Durch eine

vorsichtige Wärmebehandlung mit Lithium dargestellte Proben enthielten mehr adsorbiertes Wasser als die Original-Montmorillonite. Bei der Darstellung von RCM's reagierte ein Teil der Lithiumkationen mit Hydroxylgruppen in der oktaedrischen Schicht und setzten Protonen frei, die mit der Struktur reagierten. Eine Säurebehandlung erhöht wahrscheinlich die Ober-flächengröße, was sich in einer gesteigerten Menge an adsorbiertem Wasser wiederspiegelt. Die Deprotonierung der Hydroxylgruppen wurde durch Messungen des Glühverlustes bestätigt. Das Erhitzen von lithiumgesättigten Montmorilloniten bei höheren Temperaturen bringt den Zusammenfall der Trennschichten und eine Minderung der Menge adsorbierten Wassers mit sich.