THERMO-XRD INVESTIGATION OF MONOIONIC MONTMORILLONITES MECHANOCHEMICALLY TREATED WITH UREA

Eva Abramova, I. Lapides and S. Yariv[*]

Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

Montmorillonite (**M**) saturated with H^+, Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Co^{2+}, Cu^{2+}, Al^{3+} and Fe^{3+} were dry-ground with urea (**U**) in mass ratios **U/M** between 0.1 and 2.0 in an agate mortar and diffracted by X-ray. Extensive swellings occurred with H-, Li-, Na-, di- and trivalent cation-clays, suggesting the formation of urea-montmorillonite intercalation complexes. Mechanochemically treated samples were heated at different temperatures up to 375°C. The rise in temperature was accompanied by a decrease in the basal spacing. There was a correlation between the results of the thermo-XRD-analysis and the fine structures of the urea-montmorillonite complexes described in the literature. Five stages in the basal spacing *vs.* temperature curves were identified. In the first stage (at 150°C) the decrease was due to dehydration. In the second stage (175°C) this dehydration was accompanied by some thermal intercalation of excess urea. The other stages (at 225, 325 and 375°C) were associated with the degradation of urea and the condensation of the degraded species to polymeric products. At 375°C Li-, Na-, K-NH₄-, Mn-, Co- and Cu-montmorillonite collapsed, indicating that urea was evolved. The other urea-clay complexes did not collapse due to intercalated polymers formed by the degradation products of urea.

Keywords: *adsorption, intercalation complexes, mechanochemical adsorption, montmorillonite, thermo-XRD-analysis, urea-montmorillonite complexes*

Introduction

The mechanochemical treatment seems to be an efficient technique for adsorption of organic matter by various clay minerals [1]. Never the less the process of mechanochemical intercalation of adsorbed molecules between smectite layers is not well understood. In the mechanochemical adsorption study of organic compounds by expanding montmorillonite, the clay is ground with excess of the organic compound. Consequently, the analysis of the products should be carried out by sophisticated methods. Recently we showed that in case of cationic dyes, such as rhodamine-6G or crystal violet, the mechanochemical-adsorption took place on the external surface of the clay [2, 3]. However, by adding water to the ground mixture the cationic dye penetrated into the interlayer space. On the other hand, in case of non-ionic molecular compounds, such as phenol and its derivatives, considerable amounts of organic matter were adsorbed into the interlayer space during the grinding process. We assumed that the clay was first delaminated by the grinding process and this was followed by the formation of new tactoids with noncharged organic molecules trapped inside the newly formed interlayer space [4–6].

In the present study the mechanochemical-adsorption of urea by different mono-ionic montmorillonites and the study of the resulting organo-clay complexes by thermo-XRD-analysis is described. Urea is very important physiologically. It is the chief nitrogeneous product of protein metabolism. This compound is applied as a fertilizer and as a starting material in several industrial processes such as synthesis of formaldehyde-urea plastics, barbiturates, hydrazine and organic dyes etc. It is a proton acceptor behaving as a monoacid base [7].

IR spectroscopy study of the fine structure of amine- or amide-montmorillonite complexes revealed four types of interaction between NH_2 groups of adsorbed amines or amides and exchangeable cations [8, 9], (1) the NH_2 group of the molecular amine or amide is protonated by acidic interlayer water; (2) the NH_2 group is bonded to the exchangeable cation via a water molecule bridge attached to the N atom by H-bond in which the water molecule donates a proton; (3) the NH_2 group is bonded directly to the exchangeable cation either by donation the N-electron lone pair to the cation or by ion-dipole interaction and (4) the NH_2 group donates a proton to a basic site in the interlayer space. Applying infrared spectroscopy, Mortland [10] investigated the adsorption of urea from aqueous solutions by different monoionic montmorillonites. He identified the following three types of montmorillonite complexes of urea, the fine structure of which depended on the exchangeable cations, (1) urea protonated by acidic interlayer water; (2) mo-
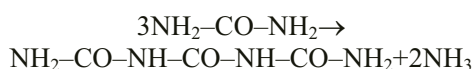
lecular urea bonded to the exchangeable cation probably via water molecule bridge and (3) molecular urea bonded directly to the exchangeable metallic cation via the CO group of urea.

To establish whether adsorbed organic molecules are located inside the interlayer space of montmorillonite, thermo-XRD-analysis is used in our laboratory [11]. Urea is expected to decompose during the thermal treatment applied for this analysis and the decomposition products may evaporate or polymerize. Mortland already in 1966 identified by IR spectroscopy the presence of trapped NH_3 obtained as a thermal decomposition product of urea at 90°C in the urea-montmorillonite complexes.

For the thermo-XRD-analysis of urea-montmorillonite complexes the knowledge on the thermal behavior of urea is essential. This knowledge is summarized here [7]. When gently heated, neat urea loses ammonia to form biuret:

$$2NH_2–CO–NH_2 \rightarrow NH_2–CO–NH–CO–NH_2+NH_3$$
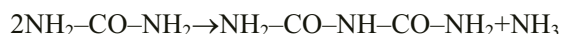
In the presence of a suitable catalyst biuret and triuret are obtained:

$$3NH_2–CO–NH_2 \rightarrow$$
$$NH_2–CO–NH–CO–NH–CO–NH_2+2NH_3$$

When heated rapidly, ammonia is evolved and urea forms cyanic acid, which rapidly trimerizes to cyanuric acid:

$$NH_2–CO–NH_2 \rightarrow H–O–C≡N+NH_3$$

$$3NH_2–CO–NH_2 \rightarrow (H–O)_3C_3N_3+3NH_3$$
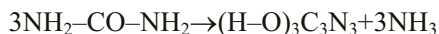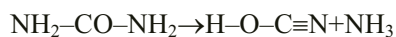
When heated rapidly in the presence of a catalyst urea evolves water and forms cyanamide, which when melted trimerizes to the cyclic compound melamine:

$$NH_2–CO-NH_2 \rightarrow NH_2–C≡N+H_2O$$

$$3NH_2–CO–NH_2 \rightarrow (NH_2)_3C_3N_3+3NH_3$$
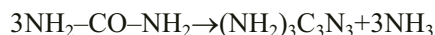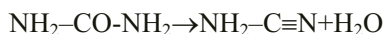
Some thermal transformations of urea and the resulting dimeric, trimeric and polymeric species are shown in Fig. 1.

The thermo-XRD-analysis does not provide information about the composition of the urea thermal products. Only the information about the thermal behavior of the montmorillonite skeleton is obtained. The purpose of the present study is to follow after thermal changes in the different monoionic urea-montmorillonite skeletons and to examine if these changes depend on the exchangeable cations and on the fine structures of the urea-montmorillonite complexes described by Mortland [10].
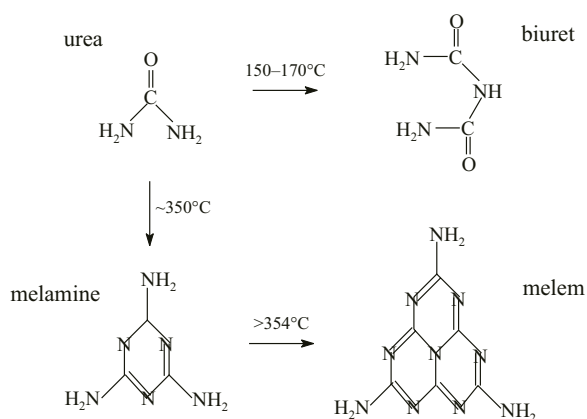

Fig. 1 Thermal transformations of urea

Experimental

Materials

Urea was supplied by Sigma and was used as received.

Na-montmorillonite (Wyoming bentonite) [12] was supplied by Wards, Natural Establishment, Inc. The clay was ground and sieved to 80 mesh. It was purified from quartz and other non-clay materials by separation of the sedimented non-colloidal fraction from a 2% aqueous suspension. Na-montmorillonite was transformed to H-, Li-, K-, Rb-, Cs-, NH_4-, Mg-, Ca-, Sr-, Ba-, Mn-, Co-, Cu-, Al- and Fe-montmorillonite by dropwise adding 40 mL of 1.0 M aqueous solution of the appropriate chloride salt to 100 mL of 1.8% suspension of the purified Wyoming bentonite. After being stirred for 24 h the excess salt was separated by dialysis with distilled water until the solution did not contain Cl^- and no precipitate was obtained with $AgNO_3$. The monoionic montmorillonites were kept in 1.0% aqueous suspensions. For each mechanochemical experiment 5.0 mL of the suspension was air-dried on a piece of polyethylene. After 24–48 h the water evaporated away and a clay film was obtained which could be readily stripped from the polyethylene and weighed and transferred into an agate mortar.

Methods

Mechanochemical treatment

The air-dried clay film (50 mg) of monoionic montmorillonite (**M**) was manually dry-ground for 5 min with urea (**U**) in an agate mortar and pestle in the mass ratios **U/M**= 0.1/1.0; 0.25/1.0; 0.5/1.0; 1.0/1.0 and 2.0/1.0 (or 167; 418; 835; 1.670 and 3.340 mmol **U** per 100 g clay, respectively).

Thermal treatment

The ground mixtures were heated in air at 150, 175, 200, 225, 325 and 375°C for 3 h at each temperature. These temperatures were chosen after preliminary experiments.

X-ray diffraction analysis

X-ray diffractograms of powdered samples before and after thermal treatment were recorded by a Philips Automatic Powder Diffractometer (PW 1710) with a Cu-tube anode at room temperature.

Results and discussion

Mechanochemical adsorption of urea by monoionic montmorillonites

An X-ray diffractogram of urea manually ground for 5 min is depicted in Fig. 2. In Fig. 3 X-ray diffractograms of Ca-montmorillonite ground for 5 min in the absence of urea and of the same clay ground with urea in mass ratios of **U/M**=0.1/1.0 and 1.0/1.0 are shown. By comparing the 001 reflection (basal spacing) of Ca-montmorillonite sample, which was ground without urea (1.50 nm) with those of the clays, which were ground in the presence of urea (1.59 and 1.67 nm, respectively), it is obvious that during the grinding process swelling of the clay occurred suggesting that urea intercalated into the interlayer space. Peaks of crystalline urea with spacings of 0.40 (very broad) and 0.36 nm were clearly detected in the diffractogram of the sample with mass ratio **U/M**=1.0/1.0, but not with mass ratio **U/M**=0.1/1.0. This is an indication that in the latter mixture most urea was adsorbed by Ca-montmorillonite but some urea remained non-adsorbed in the former mixture.

In Table 1 the basal spacings of all monoionic montmorillonites recorded after grinding without
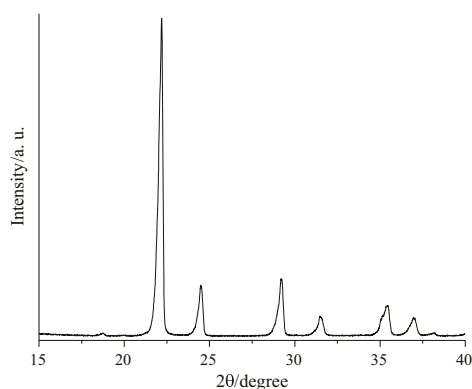
Fig. 2 X-ray diffractogram of urea manually ground for 5 min
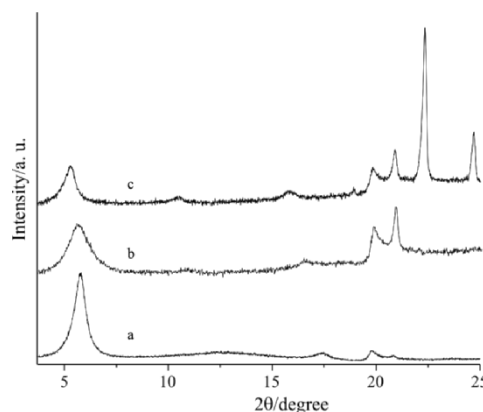
Fig. 3 X-ray diffractograms of a – Ca-montmorillonite manually ground for 5 min without urea; b, c – Ca-montmorillonite manually ground for 5 min with urea, mass ratio urea/montmorillonite b – 0.1/1.0 and c – 1.0/1.0

urea are depicted together with the basal spacings of the same clays recorded after they had been ground with urea (mass ratio **U/M**=2.0/1.0). The classification of the monoionic montmorillonites in our study into four groups is based on the three groups of urea-montmorillonite complexes, which were identified by Mortland [10] and on the fact that organo-montmorillonite complexes with exchangeable alkali cations lose water at lower temperatures compared with complexes with exchangeable alkaline earth cations [8, 9]. Very small insignificant differences in basal spacings (mostly in the range of ±0.02 nm) were sometime observed when the mass ratio **U/M** was smaller than 2.0/1.0.

The table shows extensive swelling with most exchangeable cations, indicating that considerable amounts of urea were intercalated during the mechanochemical treatment. On the other hand, the swelling of K-, Rb-, Cs- and NH$_4$-montmorillonite was limited, their spacings increased only up to 1.26 nm. These large monovalent cations are known as water structure breakers [13, 14]. Non-structured water molecules may form strong hydrogen bonds with the oxygen planes of the clay and consequently may prevent mechanical delamination, thus the extensive swelling did not occur.

All diffractograms of mixtures of the different monoionic montmorillonites with urea which initially contained mass ratios **U/M**≥0.5/1.0, showed excess residual non-adsorbed urea after the mechanochemical treatment, whereas all diffractograms of mixtures with initial mass ratios **U/M**=0.1/1.0, did not show peaks of non-adsorbed urea. Concerning diffractograms of mixtures with initial mass ratio **U/M**=0.25/1.0, all monovalent cation-, Cu- and Al-montmorillonite showed small peaks of excess non-adsorbed urea after the mechanochemical treatment, but the other did not. From these results it is ob-

Table 1 Basal spacings (in nm) of unloaded monoionic montmorillonites and of monoionic montmorillonites ground 5 min with urea (urea/montmorillonite mass ratio=2/1), before thermal treatments and after heating the samples at different temperatures up to 375°C

| Cation	Basal spacings (001 reflection)/nm							
	Montmorillonite		Montmorillonite ground with urea					
	25°C	375°C	25°C	150°C	175°C	225°C	325°C	375°C
Alkali metal cations and ammonium								
Li^+	1.26	0.96	1.57	1.41	1.44	1.28	1.24	1.03
Na^+	1.27	0.96	1.67	1.45	1.45	1.10	1.10	1.01
K^+	1.10	1.00	1.25	1.31	1.32	1.21	1.13	1.03
Rb^+	1.16	1.08	1.27	1.38	1.37	1.24	1.18	1.18
Cs^+	1.19	1.17	1.26	1.24	1.23	1.23	1.20	1.19
NH_4^+	1.16	1.00	1.27	1.38	1.34	1.22	1.15	1.04
Alkaline earth metal cations								
Mg^{2+}	1.51	0.96	1.68	1.69	1.70	1.45	1.34	1.13
Ca^{2+}	1.50	0.96	1.68	1.63	1.61	1.44	1.37	1.26
Sr^{2+}	1.44	0.99	1.73	1.60	1.59	1.52	1.30	1.26
Ba^{2+}	1.24	1.13	1.78	1.60	1.57	1.31	1.24	1.21
Transition metal cations								
Mn^{2+}	1.48	0.96	1.67	1.70	1.66	1.41	1.17	1.03
Co^{2+}	1.47	0.97	1.68	1.63	1.63	1.43	1.18	1.03
Cu^{2+}	1.22	0.96	1.66	1.48	1.47	1.27	1.14	1.03
Highly acidic cations								
H^+	1.28	0.95	1.45	1.44	1.43	1.29	1.25	1.11
Al^{3+}	1.51	0.99	1.61	1.47	1.50	1.31	1.30	1.25
Fe^{3+}	1.28	0.97	1.60	1.46	1.43	1.30	1.26	1.11

vious that the former montmorillonites are less efficient in the mechanochemical adsorption of urea compared with the other clays studied here.

Thermo-XRD-analysis of urea-montmorillonite complexes

In Fig. 4 X-ray diffractogram of Mg-montmorillonite ground in the absence of urea is depicted. The diffractogram of the same clay ground with urea in the mass ratio **U/M**=2.0/1.0 before and after gradual heating up to 375°C are also shown. Characteristic peaks of excess non-adsorbed urea were detected in the diffractogram recorded before the thermal treatment and disappeared after heating the sample at 150°C, indicating its sublimation. Basal spacing of Mg-montmorillonite was 1.51 nm. As a result of the mechanochemical adsorption of urea it increased to 1.68 nm. Similar basal spacings were recorded after the thermal treatments at 150 and 175°C. These three diffractograms showed an integral series of reflections, indicating that the urea-clay complex before and after thermal treatments up to 175°C was homogeneous.

Drastic changes were observed after heating the ground mixture at 200°C. The basal spacing dropped to 1.59 nm and the diffractogram did not show an integral series of reflections, indicating that the organo-clay sample was not homogeneous any more. With the rise in temperature of the thermal treatment the changes in the diffractograms became more pronounced and the basal spacing further decreased. After heating at 375°C the basal spacing dropped to 1.13 nm.

Curves describing the effect of thermal treatment on the basal spacing of the different monoionic montmorillonites are shown in Figs 5–8. In each figure curves belonging to one group of the urea-montmorillonite complexes are gathered. In most cases five stages can be distinguished in the basal spacings *vs.* temperature curves. In the first stage at 150°C, a significant basal spacing decrease was observed with Li-, Na-, Ca-, Sr-, Ba-, Al-, Fe-, Co- and Cu-montmorillonite, probably associated mainly with the dehydration of the interlayers. These monoionic clays showed a very intense swelling due to the mechanochemical adsorption. H- and Cs-montmorillonite showed a small decrease. No decrease was observed with Mg- and Mn-montmorillonite. K-,
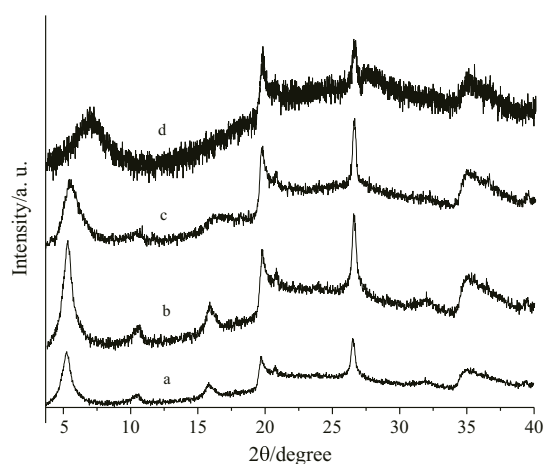
Fig. 4 X-ray diffractograms of Mg-montmorillonite manually ground for 5 min with urea, mass ratio urea/montmorillonite 2.0/1.0 a – before thermal treatment and after thermal treatments at b – 150, c – 200 and d – 375°C

Rb- and NH$_4$-clay, which during the mechano-chemical adsorption swelled very little, showed an increase in the basal spacing to 1.31–1.38 nm, probably due to thermal intercalation of urea.

In the second stage (175°C) the basal spacing decreased very slightly or did not change and in some cases even increased. It appears that at this stage two overlapping reactions occurred, dehydration of the interlayer and thermal intercalation of urea. It should be mentioned here that X-ray diffractograms of samples heated at 150°C did not show the presence of free urea. It is possible that urea which initially was present in excess, became adsorbed on the broken bonds of the clay (external surface) and at 150–175°C intercalated simultaneously with the escape of water.
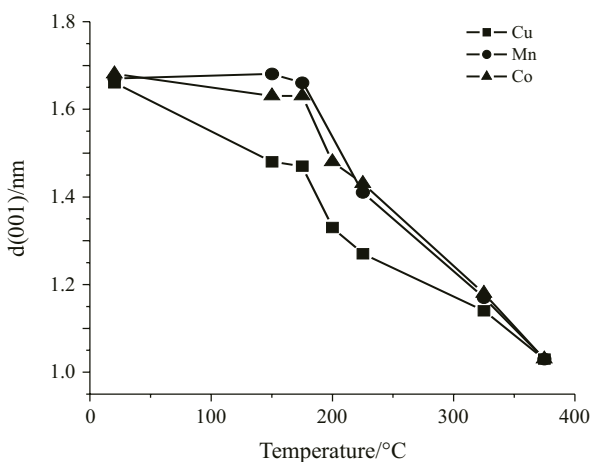
In the third stage (225°C) the thermal decrease of the basal spacing became very significant. In the
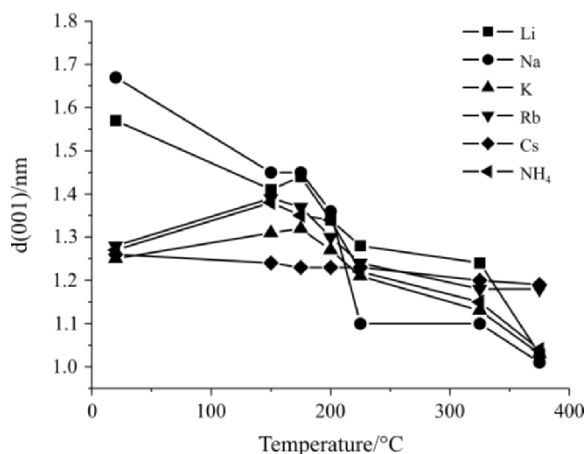
Fig. 5 The effect of temperature of the thermal treatment on the basal spacings of Li-, Na-, K-, NH$_4$-, Rb- and Cs-montmorillonite
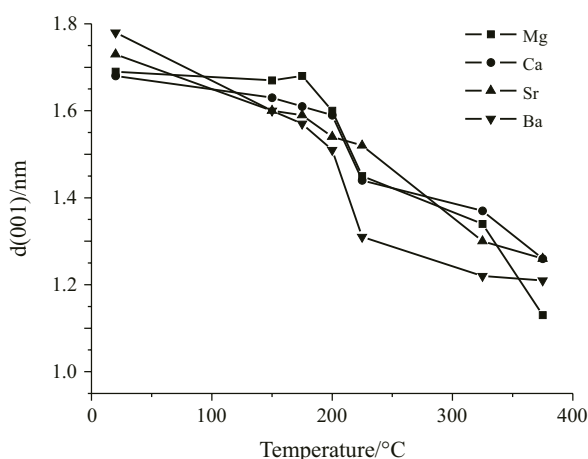
Fig. 6 The effect of temperature of the thermal treatment on the basal spacings of Mg-, Ca-, Sr- and Ba-montmorillonite

Fig. 7 The effect of temperature of the thermal treatment on the basal spacings of Mn-, Co- and Cu-montmorillonite

fourth stage (325°C) the decrease of the basal spacing became moderate. At the fifth stage (375°C) except for Rb-, Cs-, Sr- and Ba-montmorillonite, this basal spacing decrease was again pronounced. No separation to these three stages was observed with Co-, Ni- and Cu-clays. The last three stages of basal spacing decrease were probably associated with the thermal reactions of urea, the evolution of ammonia and water from urea molecules, leading to the condensation of the decomposition products to form different dimeric, trimeric and higher polymeric species. Different thermal products were obtained at various stages of the thermal treatment. The presence of different degradation and condensation products might be responsible for the different stages of the thermal treatment.

From shifts in the absorption bands of NH$_2$ and C=O groups in the IR spectra of urea in the different montmorillonite complexes, Mortland classified the urea-clay complexes obtained in aqueous suspensions at room temperature, into three groups [10]. The
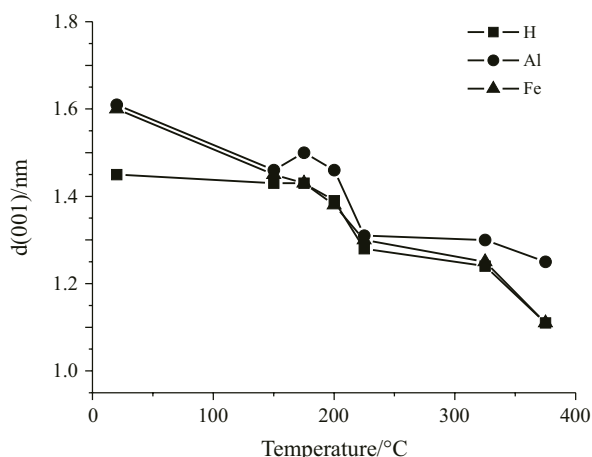
Fig. 8 The effect of temperature of the thermal treatment on the basal spacings of H-, Al- and Fe-montmorillonite
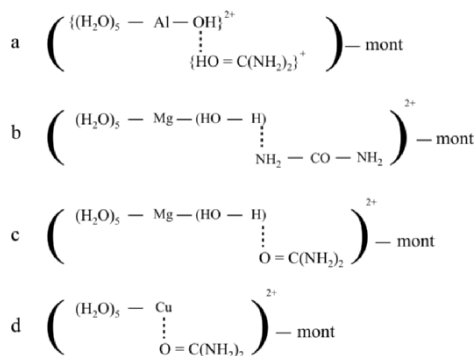
Fig. 9 Associations of urea with water and exchangeable cation in the interlayer space of montmorillonite

existence of each group depended on the exchangeable cation. In the present discussion we use the systematic classification of Mortland to explain our mechanochemical and thermal observations.

The first group in Mortland's study contained urea complexes of H-, Al- and Fe-montmorillonite. In these clays adsorbed urea was protonated by cation hydrating water inside the interlayer (Fig. 9a). The degree of protonation depended on the polarizing power of the cation, the carbonyl oxygen being the protonated site. In our study the mechanochemical adsorption of urea by these clays resulted in an extensive swelling with basal spacings of 1.45, 1.61 and 1.60 nm, respectively. At 225°C the basal spacing of H-, Al- and Fe-montmorillonite decreased to 1.3 nm (Fig. 8 and Table 1), suggesting the presence of a monolayer of the degradation products (cyanic acid and cyanamide) and the dimeric condensation product (biuret) in the interlayer space, obtained from the protonated cationic urea with the evolution of water and/or ammonia. At 325°C their basal spacing slightly dropped probably due to their trimerization to the cyclic cyanuric acid and melamin together with the evolution of ammonia. At 375°C basal spacing of

these three clays decreased to 1.11–1.25 nm suggesting that at this stage of the thermal treatment the trimeric condensation products of the protonated urea were transferred to higher polymeric products with condensed rings, such as melem.

The second group in Mortland's paper contained urea complexes of Li-, Na-, K-, Mg- and Ca-montmorillonite. According to Tahoun and Mortland [15, 16] when amides are adsorbed by montmorillonite with alkali and alkaline earth cations in ambient atmosphere, a water bridge occurs between the metallic cation and the amide. In one side the water molecule is bound to the cation by ion-dipole interaction. In its other side the water molecule is bound to the amide by H-bonds, the water molecule being the proton donor. Both functional groups of the amide, the CO and the NH_2, accept protons from the bridging water molecule (Figs 9b and c).

In our study urea complexes of alkali and alkaline earth metal cation-montmorillonites belonged to this group. The mechanochemical adsorption of urea by Mg-, Ca-, Sr- and Ba-montmorillonite resulted in an extensive swelling with basal spacings of 1.68–1.78 nm and that by Li- and Na-montmorillonite resulted with spacings of 1.57–1.67 nm. On the other hand, only a limited swelling of urea by K-, Rb-, Cs- and NH_4-clays was obtained after their grinding (Table 1). Due to the low polarizing power of K^+, Rb^+, Cs^+ and NH_4^+ the stability of the hydrated cations and their acidity are weak. Since in this group water molecules should bridge between the urea molecules and the exchangeable cations, the associations formed in the interlayers, were very unstable.

Amino-montmorillonite complexes with monovalent cations lose their water at temperatures much lower than complexes with divalent cations [8, 9]. This may explain differences in spacings between urea complexes of alkali and alkaline earth cation-clays at 175°C. Those of Mg-, Ca-, Sr- and Ba-clay were 1.57–1.68 nm, those of Li- and Na-clay 1.45 nm and those of K-, Rb-, Cs- and NH_4-clay were even smaller.

At 225°C basal spacing of Mg-, Ca- and Sr-montmorillonite decreased to 1.44–1.52 nm suggesting that at this stage urea in the interlayer space was thermally degraded with the evolution of some ammonia and water (Fig. 6). A basal spacing of ≈1.5 nm characterizes the presence of bilayers of the degradation-products in the interlayer space. At this temperature the basal spacing of Ba-montmorillonite decreased to 1.31 nm, indicating the presence of a monolayer of the degradation-products in the interlayer space. At 325°C their basal spacing dropped probably due to their trimerization to the cyclic cyanuric acid and melamin. At 375°C basal spacing of these four clays decreased to 1.13–1.26 nm suggesting that in the fifth thermal stage the cyclic trimeric conden-

sation products of urea did not evaporate but polymerized to higher condensation products with further evolution of water and ammonia molecules. The basal spacing indicates that this condensation product formed a monolayer in the interlayer space.

After the thermal dehydration, the carbonyl oxygen atom formed an ion-dipole bond with the monovalent cation and from this stage this association was responsible for the continuation of the thermal behavior of this group. With monovalent Li-, Na-, K- and NH_4-montmorillonite much of the urea was evolved from the interlayer space during the third stage of the thermal treatment (225°C), and the basal spacing at 225°C dropped to 1.10–1.28 nm (Fig. 5). It appears that the direct coordination between the carbonyl group of the urea or its thermal degradation product and the bare cation prevented the organic compound from condensation, as at 375°C the clays collapsed due to the complete evolution of the organic matter. The thermal behavior of urea complexes of this group is similar to that of complexes with transition-metal cations, as we are going to show. The thermal behavior of urea complexes of Rb- and Cs-montmorillonite is not well understood and requires more sophisticated studies.

The third group in Mortland's paper contained urea complexes of Mn-, Ni- and Cu-montmorillonite. From the IR spectra he concluded that urea was adsorbed into clays saturated with transition metal cations, by forming coordination *d*-complexes in which the CO group of the urea interacted directly with the cation (Fig. 9d). In our study this occurred with the Mn-, Co- and Cu-montmorillonite. The mechanochemical adsorption resulted in an extensive swelling with a basal spacing of 1.66–1.68 nm (Table 1). During the thermal treatment (Fig. 7) in the first stage of basal spacing decrease, the evolution of interlayer water was small with Mn^{2+} and Co^{2+}, which normally have a coordination number of 6, but relatively high with Cu^{2+}, which normally has a coordination number of 4 and forms planar complexes [17]. Above 175°C the distinction between the third, fourth and fifth thermal stages became less clear compared with that which was observed with the other urea-montmorillonite complexes. At 375°C all three montmorillonites were collapsed and the basal spacing dropped to 1.03 nm. This suggests that at this stage the urea and its thermal products were completely evolved from the interlayer space. To explain the difference in behavior between this group and the other groups of the urea-montmorillonite complexes, the stability of the coordination transition metal-urea complex should be taken into consideration. The cation-urea complex formation protected the urea from thermal conden-

sations. In the temperature range 175–375°C urea gradually evaporated from the clay.

Conclusions

Depending on the exchangeable cation, during grinding montmorillonite together with urea the latter was adsorbed by the different monoionic montmorillonites. The swelling of the clay depended on the polarizing ability of the exchangeable cation. Exchangeable cations with a high polarizing ability (H^+, Al^{3+} and Fe^{3+}) or medium polarizing ability (Li^+, Na^+, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}) and transition-metal-cations (Co^{2+}, Ni^{2+} and Cu^{2+}) led to an extensive swelling of the montmorillonite whereas cations with a low polarizing ability (K^+, Rb^+, Cs^+ and NH_4^+) led to a limited swelling.

There was a correlation between the thermal behavior of urea-clay intercalation complex and the fine structure of the complexes at room temperature. When the exchangeable cation had a high polarizing ability, the urea molecule was protonated and at 375°C polymeric products of thermal condensation were present in the interlayer space, preventing its collapse. When the exchangeable cation was divalent with a medium polarizing ability, the urea was bound to the cation via a water bridge, and at 375°C polymeric products of thermal condensation were present in the interlayer space. When the exchangeable cation was monovalent it lost its hydration water at a relatively low temperature and the urea became directly coordinated to the cation. The cation-urea association protected the urea from condensation. At 175–375°C the organic matter completely evolved and the clay collapsed. When the exchangeable cation was a transition-metal-cation urea was directly coordinated to the cation. The cation-urea complex association protected the urea from thermal condensations. In the temperature range 175–375°C urea gradually evaporated from the clay and the clay collapsed.

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