

THERMAL STUDY OF SURFACTANT AND ANION ADSORPTION ON CLINOPTILOLITE

A. D. Vujaković, M. A. Djuričić and M. R. Tomašević-Čanović

Institute for Technology of Nuclear and Other Mineral Raw Materials, Franske d'Epere Street 86,
P.O. Box 390, 11000 Belgrade, Yugoslavia

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Abstract

The mechanism of surfactant adsorption on various forms of clinoptilolite was studied by DTA, TG and DTG analyses. The examined series of surfactant modified clinoptilolite (SMC) was previously prepared by the adsorption of the surface-active oleylamine on Ca^{2+} , Na^+ , H^+ and mechanochemically treated forms of clinoptilolite. The oleylamine was most strongly adsorbed on H^+ -forms of clinoptilolite due to the largest number and strength of adsorption sites. The surfactant adsorption mechanism on H^+ -form of clinoptilolite was studied by recording the series of variously surfactant-loaded samples. The products of sulphate, dihydrogenphosphate and hydrogenchromate adsorption on SMC were analyzed by DTA, TG and DTG in order to investigate the mechanism of anion adsorption.

Keywords: acid sites, adsorption, anion, clinoptilolite, H^+ -form, oleylamine, surfactant, thermal analysis

Introduction

Thermal analyses are commonly used for the investigation of numerous types of amine–clay complexes [1]. The interpretations of the interactions between the amine and the clay mineral can be as well applied in revealing the interactions between the amine and the zeolite. The layered structure of clay minerals on one hand and the cage-like structure of zeolites on the other, must certainly be considered. The amine adsorption on zeolites was extensively investigated in the field of catalysis [2, 3]. The alkyl and aromatic amines have been adsorbed on synthetic and natural zeolites [4]. The adsorption–desorption studies gave the decisive contribution to understanding of the zeolite acid sites [5]. The new and yet not enough investigated aspect of amine adsorption on zeolites is the use of amine–zeolite complexes in the field of environmental pollution. In recent years, researches have been done on the adsorption of organic [6] and anion pollutants on zeolites modified by surface-active amines. The anion adsorption on zeolites was investigated by Bowman and co-workers [7]. The anion adsorbent was prepared by the cation exchange with the surface-active ammonium salt

at external zeolite surface. However, the authors of the present study presumed that anion adsorption might be improved by altering the clinoptilolite properties as well as by choosing another surfactant type. Therefore, the modification of natural clinoptilolite was performed as was described in previous study [8]. The influence of cation type and crystallinity degree on amine and anion adsorption was investigated. An attempt was made to prepare the most efficient zeolite-based anion adsorbent. It was found that H^+ -clinoptilolites exhibited the superior amine and anion adsorption. This study aimed at elucidating the mechanism of amine and anion adsorption on variously modified clinoptilolite by use of DTA, TG and DTG analysis.

Materials and methods

Materials

The starting material for the preparation of SMC was the clinoptilolite-rich tuff from the deposit Zlatokop (Vranje), Yugoslavia. The content of clinoptilolite is higher than 85%, with pyrite, quartz and feldspar as major impurities [9]. The raw material was ground and wet-classified to <0.063 mm. This clinoptilolite tuff is predominantly the calcium type with the total cation exchange capacity, $CEC=1420$ meq kg^{-1} , and the external cation exchange capacity, $ECEC=190$ meq kg^{-1} . The samples were prepared and characterized as described in previous study [8]. A summary of various forms of clinoptilolite prepared and their corresponding SMC samples are given in Table 1.

Table 1 Properties of examined clinoptilolite samples: cation forms and amount of oleylamine added for organo-zeolite preparing

Sample	Treatment of natural clinoptilolite	Cation-form	Surfactant added/ mmol kg^{-1}	SMC sample
Z	untreated	Ca^{2+}	190	OZ
HZ-1	0.005 M HCl	23% H^+	190	OHZ-1
			95	OHZ-2/1
			190	OHZ-2/2
HZ-2	1 M HCl	70% H^+	285	OHZ-2/3
			380	OHZ-2/4
			1140	OHZ-2/5
			1900	OHZ-2/6
HZ-3	0.5 M NH_4Cl , calcined at $400^\circ C$	95% H^+	190	OHZ-3
NaZ	0.5 M NaCl	Na^+	190	ONaZ
MCZ	mechanochemical	Ca^{2+}	190	OMCZ

The oleylamine supplied by Akzo Chemie was used for the preparation of SMC samples. This organic base is primary, long chained fatty amine with one unsaturated bond at the ninth carbon atom. Its relative molecular mass is 267.5 g mol^{-1} , it is insoluble in water and readily soluble in polar and non-polar organic solvents, with flash

point at 160°C. It can be seen in Table 1 that the oleylamine was added to clinoptilolite samples in the quantities equivalent to the *ECEC* value, except for the OHZ-2 sample with various oleylamine additions.

The SO_4^{2-} , H_2PO_4^- and HCrO_4^- adsorption experiments were carried out on SMC sample OHZ-2/2, as described in previous study [8]. The adsorption complexes anion/SMC were examined by DTA, TG and DTG techniques. These samples are designated OHZ-2/2/ SO_4^{2-} , OHZ-2/2/ H_2PO_4^- and OHZ-2/2/ HCrO_4^- .

Methods

The Netzsch STA 409 EP was used for DTA, TG and DTG analyses of SMC samples. Samples were heated in an air atmosphere, in the temperature range 20–700°C, with the heating rate 5°C min⁻¹.

Results and discussion

The results of the thermal analysis of the clinoptilolite and SMC samples are summarized as follows. The mass losses for the various forms of clinoptilolite and for corresponding SMC samples can be observed in Table 2.

Table 2 Mass losses of the clinoptilolites and their corresponding SMC samples in dehydration (20–200°C) and oleylamine desorption and oxidation (200–700°C) temperature range

Sample	Mass loss/%		
	20–200°C	200–700°C	Σ 20–700°C
Z	6.7	5.8	12.5
OZ	5.9	7.2	13.1
HZ-1	6.9	6.6	13.5
OHZ-1	5.6	7.6	13.2
HZ-2	8.6	4.6	13.2
OHZ-2/2	6.6	6.6	13.2
HZ-3	6.5	5.1	11.6
OHZ-3	6.0	7.6	13.6
MCZ	7.1	4.8	11.9
OMCZ	6.1	7.8	13.9
NaZ	6.1	5.2	11.3
ONaZ	5.7	7.4	13.1

Two temperature regions are distinguished in Table 2, the region of zeolitic water loss (20–200°C) and the region of oxidation of organic substance (200–700°C). In the first temperature region the mass losses of clinoptilolite samples do not differ significantly, except for the sample HZ-2 with partially dealuminated crystal lattice. The higher mass loss in the dehydration region for dealuminated clinoptilolite is in accordance with literary data [10]. It can be seen in Table 2 that the mass losses of the SMC samples decreased in the first temperature region. It can be ascribed to the increased

hydrophobicity of the SMC samples. In the second temperature range 200–700°C, the mass loss of SMC increased due to oxidation of surface-active oleyamine.

The TG, DTG and DTA curves for the starting clinoptilolite (Z) and for the corresponding SMC sample (OZ) are presented in Fig. 1.

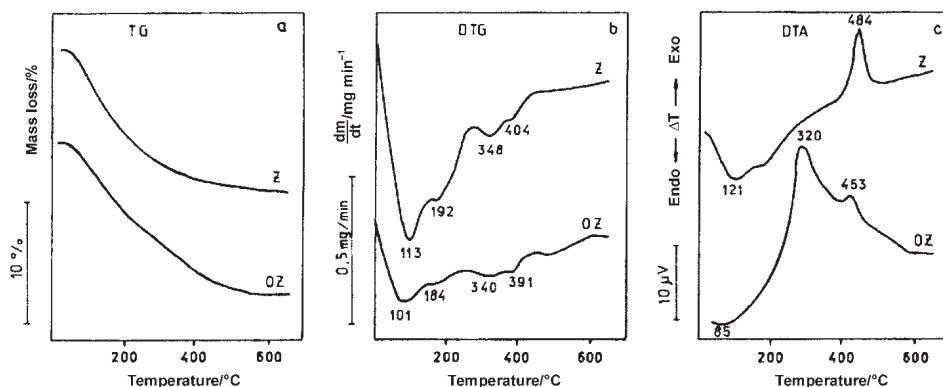


Fig. 1 TG (a), DTG (b) and DTA (c) curves for the starting clinoptilolite (Z) and for the SMC sample (OZ)

The TG curves for Z and OZ samples themselves do not differ significantly (Fig. 1a). The curve Z in DTG diagram (Fig. 1b), with triple derivative peak, is characteristic for the Ca-clinoptilolite [11]. This strong derivative peak is significantly weakened for OZ sample. The DTA curve Z (Fig. 1c), with pyrite oxidation peak at 484°C is characteristic for the Ca-clinoptilolite from the Zlatokop deposit, Yugoslavia. DTA curve for OZ displays the dehydration endotherm with lowered peak temperature as well as the broad exothermic peak corresponding to the oleyamine oxidation. The pyrite oxidation peak is observed and is lowered to 453°C.

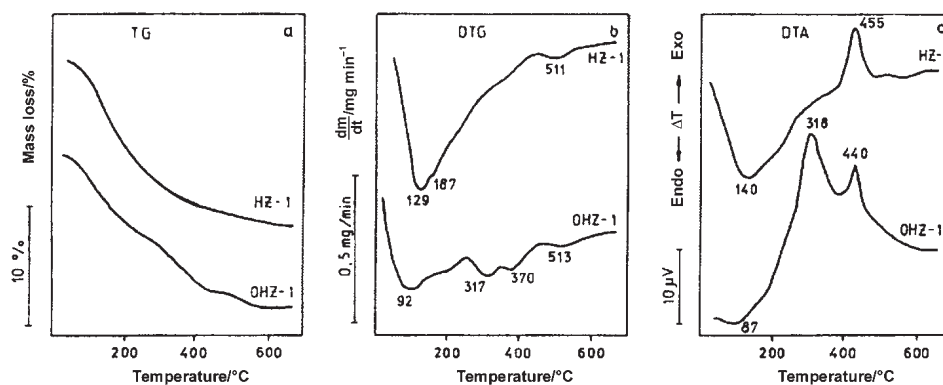


Fig. 2 TG (a), DTG (b) and DTA (c) curves for the H⁺-clinoptilolite (HZ-1) and for the SMC sample (OHZ-1)

The TG curve for OHZ-1 (Fig. 2a), differs in slope from the curve HZ-1. The slower mass loss for OHZ-1 in the first temperature region and the faster one in the second region may be observed. It is in accordance with lowered intensity of the first derivative peak for the OHZ-1 sample (Fig. 2b), and with appearance of two derivative peaks at 317 and 370°C. The DTA curves for the HZ-1 and OHZ-1 can be seen in Fig. 2c. DTA curve for the HZ-1 differs from the one for the starting clinoptilolite Z (Fig. 1c). No characteristic Ca-shoulder is observed on dehydration peak, and the pyrite oxidation peak temperature is lowered to 455°C, due to the treatment with weak HCl solution (Table 1). A lower dehydration peak and a broad exothermic peak with a maximum at 318°C may be observed in DTA curve for the OHZ-1. The pyrite oxidation peak is further lowered to 440°C.

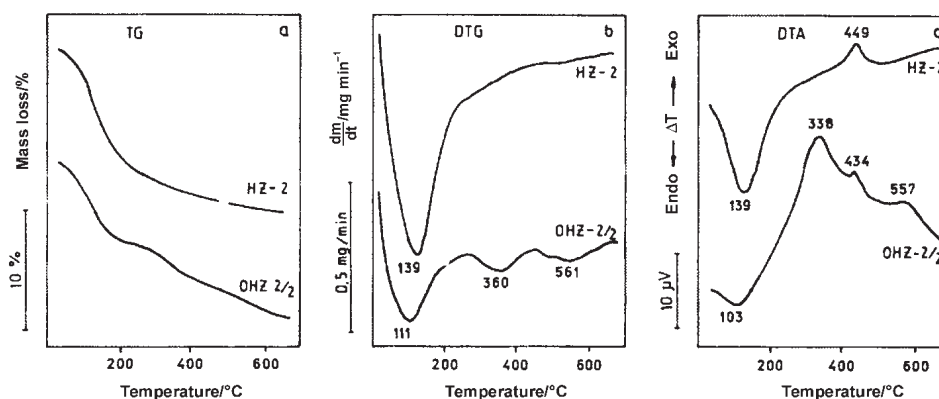


Fig. 3 TG (a), DTG (b) and DTA (c) curves for the H^+ -clinoptilolite (HZ-2) and for the SMC sample (OHZ-2/2)

The difference in slope of TG curves HZ-2 and OHZ-2/2 (Fig. 3a), is in accordance with the difference in the mass loss data in Table 2. This is also confirmed by significant decrease in dehydration derivative peak intensity as well as by the appearance of the new high-temperature derivative peaks for the OHZ-2/2 sample (Fig. 3b). Dehydration endotherm with no traces of exchangeable Ca and the pyrite oxidation peak with lowered intensity and temperature (449°C) are the results of treatment with strong HCl solution, curve HZ-2 (Fig. 3c). The lowered dehydration peak temperature and the broad oleylamine oxidation exotherm can be observed on DTA curve for the sample OHZ-2/2. Two stages for exothermic oxidation of the surfactant adsorbed by the zeolite (338 and 557°C), as well as the pyrite oxidation peak (434°C) are distinguished. The increase of oleylamine oxidation peak temperature from 320 for OZ (Fig. 1c) to 338°C for OHZ-2/2 and the appearance of the new peak at 557°C are the indication of stronger bonding between the oleylamine and H^+ -clinoptilolite. It is known that the location of the first peak depends on the organic amine and on the type of bonding between the mineral and the amine [12]. The location of the second peak

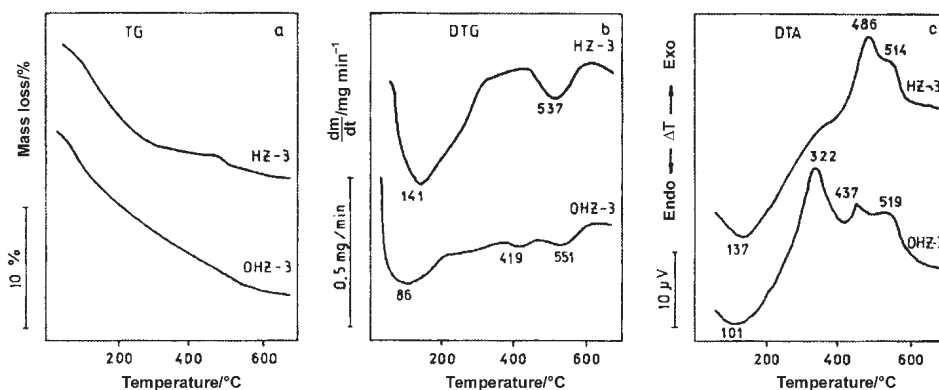


Fig. 4 TG (a), DTG (b) and DTA (c) curves for the H^+ -clinoptilolite (HZ-3) and for the SMC sample (OHZ-3)

also depends on the type of bonding, because the type of charcoal, which is formed during the first stage, is dependent on these factors.

The mass loss at 537°C for the HZ-3 sample in Fig. 4a corresponds to the oxidation of remained ammonia. It is not observable on TG curve for the OHZ-3 sample because it coincides with the mass loss from the oxidation of oleylamine. However, these two processes are well distinguished on DTG diagram, (Fig. 4b), curve OHZ-3. DTA curve for HZ-3, (Fig. 4c), differs from the starting one (Z) (Fig. 1c), in overlapping the pyrite and ammonia oxidation exotherms. It can be observed that the intensity and temperature of pyrite peak remained unchanged for this clinoptilolite with undamaged crystal structure. The curve OHZ-3 for the SMC sample displays dehydration peak at lower temperature than for HZ-3 and the broad exotherm with oleylamine (322°C), pyrite (437°C) and the ammonia (519°C) oxidation peaks. The

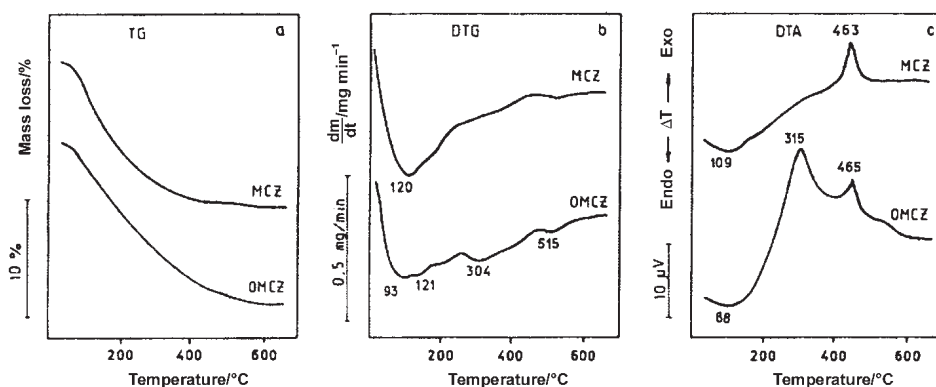


Fig. 5 TG (a), DTG (b) and DTA (c) curves for the mechanochemically treated clinoptilolite (MCZ) and for the SMC sample (OMCZ)

ammonia oxidation peak might coincide with the second oxidation peak of oleylamine.

TG curves for the MCZ and OMCZ samples differ in slope (Fig. 5a), due to different mass losses (Table 2). If we compare the DTG curve for the starting clinoptilolite sample (Z) (Fig. 1b), with the one for MCZ (Fig. 5b), the decreased intensity of dehydration derivative peak for the MCZ may be observed. It points to the damaged structure of MCZ sample. The three shoulders characteristic for Ca-clinoptilolite may be noticed. The evidence of the damaged structure can also be observed in DTA curve for MCZ (Fig. 5c), with decreased intensity and temperature (463°C) of pyrite peak. The presence of the organic phase may be observed on DTG and DTA curves for OMCZ sample with recognizable oleylamine oxidation (315°C) and pyrite (465°C) peaks.

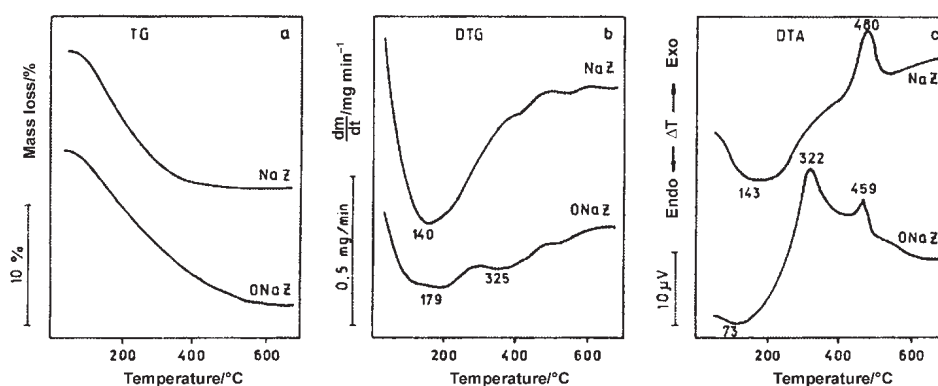


Fig. 6 TG (a), DTG (b) and DTA (c) curves for the Na-clinoptilolite (NaZ) and for the SMC sample (ONaZ)

The significant difference in derivative dehydration peak intensity can be observed between the NaZ and ONaZ sample (Fig. 6b), due to the increased hydrophobicity of SMC sample. The DTA curve for the NaZ sample (Fig. 6c), shows the broad Na-characteristic endotherm at 143°C and the pyrite oxidation peak with unchanged intensity and temperature (480°C). The presence of organic phase on ONaZ induces the lower intensity and temperature of dehydration peak (73°C) and the appearance of broad exotherm with oleylamine oxidation peak at 322°C. The pyrite oxidation peak is shifted to 459°C.

The appearance of the third small exothermic peak at temperature $>500^\circ C$ can be observed only for the samples OHZ-2 and OHZ-3. This is an indication of the presence of another type of association between the surfactant and zeolite. It was observed in previous study [8] that the oleylamine was the most strongly adsorbed one on H^+ -zeolites. Therefore, more extensive thermal study was performed on SMC based on H^+ -form of clinoptilolite that was obtained by the treatment with the 1 M HCl solution. The type of bonding was tried to be evaluated by recording the SMC

with various quantities of oleylamine adsorbed. The mass losses for the series of SMC based on H⁺-form of clinoptilolite with oleylamine additions equivalent to 50–1000% *ECEC* are presented in Table 3. The decrease in mass loss in the first temperature region 20–200°C may be associated with increased hydrophobicity. For two samples with large excess of oleylamine, the oxidation of weakly bound excess oleylamine starts already in this temperature range. In the second temperature region 200–700°C, two-step mass loss can be observed for the series of SMC. The mass loss is caused by oxidation of organic material and increases with the increase of the amount of oleylamine adsorbed.

Table 3 Mass losses of the H⁺-based SMC samples with various loading of oleylamine in dehydration (20–200°C) and oxidation (200–700°C) temperature range

Sample	Oleylamine added/ % <i>ECEC</i>	Mass loss/%		
		20–200/°C	200–700/°C	∑ 20–700/°C
OHZ-2/1	50	6.7	5.3	12.0
OHZ-2/2	100	6.6	6.6	13.2
OHZ-2/3	150	5.6	8.7	14.3
OHZ-2/4	200	5.6	12.2	17.8
OHZ-2/5	600	6.4	17.3	23.7
OHZ-2/6	1000	6.5	20.4	26.9

The TG, DTG and DTA diagrams for the series of variously oleylamine loaded H⁺-clinoptilolite are given in Fig. 7.

The intensities of DTG peaks in the temperature region 20–200°C decrease in the series of SMC as the zeolitic water content decreases (Fig. 7b). DTG peaks for the most hydrophobic samples OHZ-2/5 and OHZ-2/6 split into two small peaks and almost disappear. Two DTG peaks confirm that the mass loss in the temperature region of oxidation of organic compound occurs in two steps. In DTA diagram (Fig. 7c), the endothermic peaks can be observed in the first temperature region 20–200°C, corresponding to the loss of zeolitic water. The endothermic peak temperatures for the series of SMC are lower than for the starting zeolite sample, due to the increased surface hydrophobicity. The DTA curves in the exothermic temperature region 200–700°C give details on oleylamine bonding on zeolite surface (Fig. 7c). The curve OHZ-2/1 in Fig. 7c corresponds to the SMC with oleylamine additions 9.5 mmol kg⁻¹, which equals 50% of the *ECEC* of clinoptilolite. It means that half of the available active sites at external zeolite surface is covered by oleylamine. Three exothermic peaks can be distinguished for this sample with low concentration of oleylamine. The broad peak at 343°C and the shoulder at 480°C correspond to oxidation of oleylamine in two stages. The sharp exotherm at 436°C is the pyrite oxidation peak. The curve OHZ-2/2 shows the thermal reactions of organic substance for the SMC with fully covered external surface. The peak at 338°C is more intensive than the peak at 343°C for OHZ-2/1 sample, while the pyrite oxidation peak at 434°C is partially overlapped

and less intensive than for sample OHZ-2/1. When the external zeolite surface is fully covered, the oleylamine continues to adsorb in multilayers. The shoulder at 205°C at the DTA curve for the sample OHZ-2/3 is the first indication of such physisorbed oleylamine. The progressive increase in the intensity of the peak at 338°C can be observed, as well as the gradual overlapping of the pyrite peak at 416°C. The peak at 565°C is still observable. The shoulder at 205°C for the sample OHZ-2/3 turned to peak at 210°C for the sample OHZ-2/4. The exothermic peak at 341°C becomes more intensive and overlaps the one around 560°C corresponding to charcoal desorption. The pyrite peak at 431°C is still distinct. For the samples with large excess of oleylamine, OHZ-2/5 and OHZ-2/6, the peaks corresponding to the oxidation of physisorbed oleylamine at 219 and 222°C, respectively, are sharp and intense. Since the oleylamine concentration became high, the exothermic peak at 349°C for the OHZ-2/5 and 342°C for the OHZ-2/6 become so large and broad that it overlaps all the other effects.

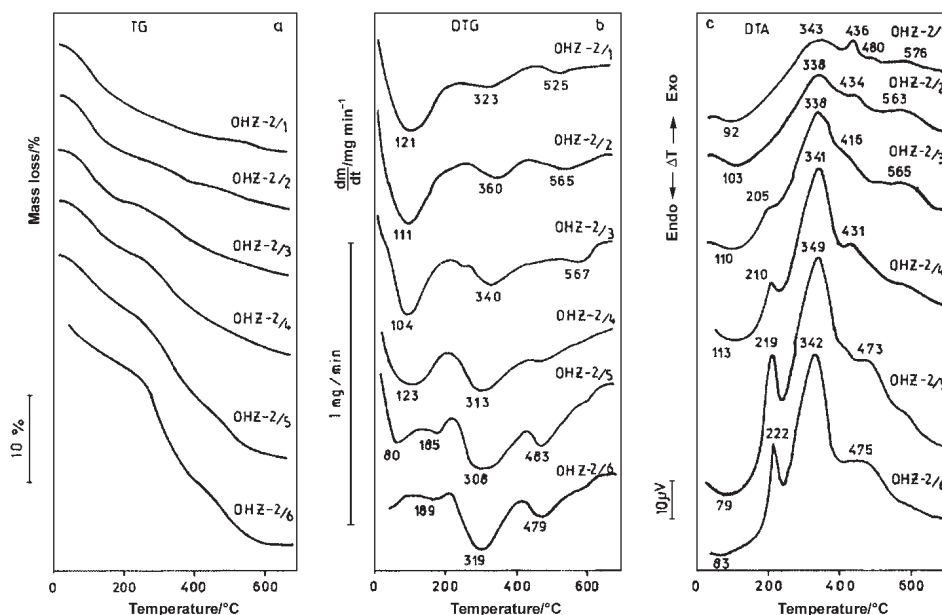


Fig. 7 TG (a), DTG (b) and DTA (c) curves for the SMC based on H^+ -clinoptilolite with oleylamine additions equivalent to: OHZ-2/1 (50% ECEC), OHZ-2/2 (100% ECEC), OHZ-2/3 (150% ECEC), OHZ-2/4 (200% ECEC), OHZ-2/5 (600% ECEC), OHZ-2/6 (1000% ECEC)

The anion adsorption experiments showed that the SMC based on H^+ -form of clinoptilolite that was obtained by treatment with the 1 M HCl solution (sample OHZ-2/2) is the most efficient adsorbent of SO_4^{2-} , $H_2PO_4^-$ and $HCrO_4^-$ anions [10]. In order to elucidate the mechanism of anion adsorption, the thermal analysis of anion

adsorption complexes was performed. The mass losses for the sample OHZ-2/2 and for anion adsorption complexes are given in Table 4.

Table 4 Mass losses of anion adsorbent OHZ-2/2 and anion adsorption complexes with sulphate, phosphate and chromate in dehydration (20–200°C) and oleylamine oxidation (200–700°C) temperature range

Sample	Mass loss/%		
	20–200/°C	200–700/°C	∑ 20–700/°C
OHZ-2/2	6.6	6.6	13.2
OHZ-2/2SO ₄ ²⁻	5.7	7.6	13.3
OHZ-2/2H ₂ PO ₄ ⁻	5.6	7.0	12.6
OHZ-2/2HCrO ₄ ⁻	5.4	9.9	15.3

The TG, DTG and DTA curves of anion adsorbent OHZ-2/2 and anion adsorption complexes with sulphate, dihydrogenphosphate and hydrogenchromate are presented in Fig. 8.

In the temperature region 20–200°C, the difference between the mass losses of anion adsorbent and anion adsorption complexes can be observed in Table 4 and in Fig. 8a. The decrease of mass loss for anion adsorption complexes indicates the substitution of zeolitic water by the anion adsorption complex. In the temperature region 200–700°C the increase of mass losses for the anion adsorption complexes, (curves

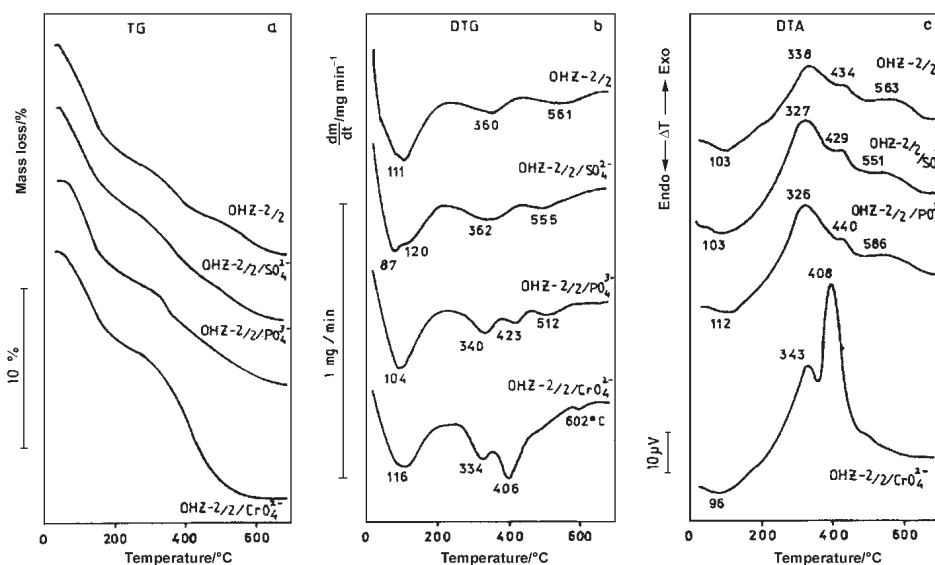


Fig. 8 TG (a), DTG (b) and DTA (c) curves for the anion adsorbent OHZ-2/2 and anion adsorption complexes with: OHZ-2/2/SO₄²⁻–sulphate, OHZ-2/2/H₂PO₄⁻–phosphate and OHZ-2/2/HCrO₄⁻–chromate

OHZ-2/2/SO₄²⁻, OHZ-2/2/H₂PO₄⁻ and OHZ-2/2/HCrO₄⁻ in Fig. 8a) may be observed. The most significant mass loss occurred for the HCrO₄⁻ adsorption complex (Table 4). The mass losses in the temperature region 20–200°C are accompanied with large DTG peaks at about 100°C (Fig. 8b). The DTG curves of anion adsorption complexes differ from those for the anion adsorbent OHZ-2/2 (Fig. 8b), especially in the temperature range 200–700°C. The peaks at 360 and 560°C at the curve OHZ-2/2 refer to the different rate of oxidation of oleylamine, in two stages. The new DTG peaks appeared for the anion adsorption complexes, indicating different kinetics of desorption. The first DTG peak in this temperature region at 362°C is weak and broad for sulphate adsorption complex, quite like the starting adsorbent (OHZ-2/2). But for dihydrogenphosphate and hydrogenchromate adsorption complexes, this peak turns to the sharper one at 340 and 334°C, respectively. For the dihydrogenphosphate adsorption complex, the sharp medium peak at 340°C is followed by the weak one at 423°C, which might be an indication of the existence of dihydrogenphosphate–SMC adsorption complex. The sharp and intensive DTG peak at 406°C appears for the hydrogenchromate adsorption complex pointing to the strong hydrogenchromate–SMC bonding.

DTA endothermic peaks in the temperature region 20–200°C are weak and broad with maxima at about 100°C (Fig. 8c). The DTA curves for the adsorbent OHZ-2/2 and anion adsorption complexes in the temperature region 200–700°C show significant differences in oxidation reactions (Fig. 8c). The DTA curves for sulphate and dihydrogenphosphate adsorption complexes exhibit much the same exothermic peaks, but larger peak areas than the DTA curve for the adsorbent. It is in agreement with the slightly increased mass losses for this two adsorption complexes. The DTA curve for the hydrogenchromate adsorption complex is quite different. The first smaller exothermic peak at 343°C can be ascribed to the oxidation of oleylamine. The second, very strong exothermic peak, at 408°C most likely results from oxidation of very stable complex between hydrogenchromate and oleylamine on zeolite surface. It was already shown in previous anion adsorption study [8] that, among these three examined anions, hydrogenchromate forms the most stable complex with SMC. The results of thermal analysis of anion adsorption complexes prove the existence of the strong hydrogenchromate–SMC complex and therefore are in agreement with the results of anion adsorption study.

Conclusions

Thermal study of different forms of clinoptilolite (Ca⁺⁺, Na⁺, Ca⁺⁺/H⁺, H⁺ and mechanochemically treated Ca⁺⁺) and their SMC analogues showed that the thermal behaviour of SMC is greatly influenced by clinoptilolite cationic and structural form. Different dehydration and oleylamine oxidation data were obtained for various SMCs. Oleylamine oxidation for three H⁺-clinoptilolites with various degree of H⁺-saturation took place at higher temperatures than for the Ca- and Na-clinoptilolites. Two stages oleylamine oxidation was observed for SMCs based on H⁺-clinoptilolites. This data point to the existence of different type of oleylamine bonding on H⁺-clinoptilolites on one hand, and Ca-

and Na-clinoptilolites on the other. Greater number and strength of adsorption sites enable H^+ -clinoptilolite to form stronger SMC with superior properties of anion adsorption. Thermal analysis of anion-SMC complexes provide the evidence for the formation of hydrogenchromate-SMC adsorption complex.

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