

Thermal transformations in systems based on zeolites Y, X, and A containing zinc and sodium nitrates

N. Ya. Usachev,* E. P. Belanova, I. M. Krukovsky, S. A. Kanaev, O. K. Atal'yan, and A. V. Kazakov

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (095) 135 5328. E-mail: ny@ioc.ac.ru

Thermal transformations in systems formed by interaction of Zn and Na nitrates with Y, X, and A zeolites were studied by TG–DTA technique. Temperature regions of existence of adsorbed water, water of crystallization, and decomposition of NO_3^- anion were determined. These intervals depend on the composition, structure, method of preparation, and pre-treatment conditions of zeolite systems. The extent of NO_3^- decomposition depends not only on the zinc and sodium content but also on the presence of ammonia involved in NO_3^- reduction. The zeolite matrix strongly stabilizes the occluded NO_3^- anions. A portion of zinc oxide formed by zinc nitrate decomposition is probably localized inside the zeolite cavities as the $[\text{Zn}—\text{O}—(\text{ZnO})_n—\text{Zn}]_2^+$ particles. The latter compensate charges of the isolated $[\text{AlO}_4]^-$ tetrahedra.

Key words: zeolites, sodium nitrate, zinc nitrate, ion exchange, thermal transformations, TG–DTA method.

An interest in zeolite-based systems has sharply increased in recent years due to the development of new composite materials containing nanoparticles of oxides, sulfides, and other compounds.^{1–3} The most popular method for synthesis of such systems includes the thermal decomposition of salts incorporated into zeolite crystals. Using this method, we have prepared several groups of non-acidic zeolites containing ZnO , which are active catalysts in the dehydrogenation of methanol to formaldehyde.^{4,5} The $\text{Zn}(\text{NO}_3)_2/\text{ZnNaZ}$ systems (Z is zeolite) prepared by impregnation of the ion-exchange forms of zeolites Y and X with a solution of zinc nitrate are most efficient in this process. Their high catalytic activity is associated with a highly dispersed ZnO phase formed by the temperature-programmed reduction of the nitrate ions by MeOH vapor. The product distribution of non-oxidative dehydrogenation of methanol at 300–500 °C in effluent collected during the first 2 h depends strongly on the NO_3^- ion content in the samples. Therefore, thermal transformations in the systems containing $\text{Zn}(\text{NO}_3)_2$ and NaNO_3 and zeolites Y, X, and A were studied by the TG–TDA method to establish thermal stability of the nitrate anions and regularities of formation of the ZnO phase.

Experimental

Two groups of zinc-containing samples were prepared. The first group based on NaY zeolites ($\text{Si}/\text{Al} = 2.2$), NaX

($\text{Si}/\text{Al} = 1.25$), and NaA ($\text{Si}/\text{Al} = 1.0$) was made by impregnation of their powders with an aqueous or aqueous-ammonia solution of zinc nitrate. According to this method, zeolite (10 g) was impregnated with an aqueous or 25% aqueous-ammonia solution (17 mL) containing $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (14 g). The second group of samples was prepared from zeolites Y and X in which 70% of the Na^+ cations were pre-substituted by the Zn^{2+} cations according to a previously published procedure.⁵ These ZnNaY and ZnNaX zeolites were impregnated by an aqueous solution of NaNO_3 (molar ratio Na^+ (salt)/ $\text{Zn}^{2+} = 2$) and an aqueous or aqueous-ammonia solution of $\text{Zn}(\text{NO}_3)_2$. The impregnated samples were dried for 2 h at 100 °C and then stored in air at 20 °C for saturation with water vapor to a constant weight. It has been established in special experiments that HNO_3 is not removed upon drying and, hence, the NO_3^- amount in such systems corresponds to the amount of introduced nitrate. A weighed sample of each sample was heated in air in a muffle furnace for 2 h, while the temperature was increased from 20 to 500 °C for 2 h. The samples were then stored for 2 h at 500 °C, cooled, and left in air at 20 °C. All reagents used were analytical purity grade. The compositions of the initial zeolites and related systems calculated on the dry basis are presented in Table 1.

The starting components and zeolite systems were studied by thermogravimetry on a Derivatograph-C instrument (MOM) in alundum crucibles with temperature-programmed heating (10 °C min^{−1}) in air. The sample weight was 20–30 mg. The standard was $\alpha\text{-Al}_2\text{O}_3$. The content of H_2O (or $\text{H}_2\text{O} + \text{NH}_3$) and NO_x was calculated from the weight loss of the samples.

Several parameters characterizing thermal properties of the samples were derived from measurements.

The fraction of NO_x (rel.%), remained in the samples after heating above 500 °C, was determined as the ratio of the high-

Table 1. Composition of the starting zeolites and related systems (dry basis)

Sample	Method of preparation	Content (mol.%)			
		ZnO	Na_2O	Al_2O_3	SiO_2
ZnNaY	Ion exchange in NaY treated with a solution of $\text{Zn}(\text{NO}_3)_2$	10.9	4.7	15.6	68.8
ZnNaX	Ion exchange in NaX treated with a solution of $\text{Zn}(\text{NO}_3)_2$	15.6	6.7	22.2	55.5
$\text{Zn}(\text{NO}_3)_2/\text{NaY}$	Impregnation of NaY with a solution of $\text{Zn}(\text{NO}_3)_2$	13.6	13.6	13.6	59.2
$\text{Zn}(\text{NO}_3)_2/\text{NaX}$	Impregnation of NaX with a solution of $\text{Zn}(\text{NO}_3)_2$	14.1	19.1	19.1	47.7
$\text{Zn}(\text{NO}_3)_2/\text{NaA}$	Impregnation of NaA with a solution of $\text{Zn}(\text{NO}_3)_2$	14.3	21.4	21.4	42.9
$\text{NaNO}_3/\text{ZnNaY}$	Impregnation of ZnNaY with a solution of NaNO_3	9.9	14.1	14.1	61.9
$\text{NaNO}_3/\text{ZnNaX}$	Impregnation of ZnNaX with a solution of NaNO_3	13.5	19.2	19.2	48.1
$\text{Zn}(\text{NO}_3)_2/\text{ZnNaY}$	Impregnation of ZnNaY with a solution of $\text{Zn}(\text{NO}_3)_2$	24.5	3.9	13.2	58.4
$\text{Zn}(\text{NO}_3)_2/\text{ZnNaX}$	Impregnation of ZnNaX with a solution of $\text{Zn}(\text{NO}_3)_2$	27.8	5.7	19.0	47.5

temperature weight loss to the weight content of NO_x in the corresponding non-calcined samples (see below). The composition of zinc nitrate was expressed, for convenience, as zinc and nitrogen oxides ($\text{ZnO} \cdot \text{N}_2\text{O}_5$), and the weight of dehydrated zeolite was taken as 100%.

$$[\text{NO}_x]_{\text{rel}} = \frac{M_{\text{ZnO}} \Delta m_2 (100 + m)}{M_{\text{N}_2\text{O}_5} m (100 - \Delta m)} \cdot 100,$$

where M_{ZnO} and $M_{\text{N}_2\text{O}_5}$ are the molar weights of ZnO and N_2O_5 (g mol^{-1}); $\Delta m = \Delta m_1 + \Delta m_2$ (%), Δm_1 is the weight loss on heating from 20 to 500 °C (%), Δm_2 is the weight loss on heating from 500 to 1000 °C (%); m is the weight fraction of ZnO in the calcined samples (%) (the zeolite content was taken as 100%, Table 2).

The content of NO_x and H_2O (wt.%) in the non-calcined samples was determined from the equations

$$[\text{NO}_x] = 100 \Delta m_2 / [\text{NO}_x]_{\text{rel}},$$

$$[\text{H}_2\text{O}] = \Delta m - [\text{NO}_x].$$

The content of H_2O and NO_x (wt.%) in the calcined samples was taken equal to Δm_1 and Δm_2 , respectively.

The water content of the zeolite component ((g of H_2O) (g of zeolite) $^{-1}$) in the calcined samples was calculated using the expression

$$[\text{H}_2\text{O}]_z = \frac{\Delta m_1 (100 + m)}{100 (100 - \Delta m)}.$$

As in the calculation of $[\text{NO}_x]_{\text{rel}}$, the weight of dehydrated zeolite was accepted to be 100%. The weight of ZnO in the sample composition was also taken into account (see Table 2).

Results and Discussion

Dehydration of the sodium forms of zeolites (NaZ) and the ion-exchange ZnNaZ samples is accompanied by the pronounced endothermic effects in the DTA curves (100–300 °C), which are characteristic of aqueous crystalline aluminosilicates.^{6,7} The shape and position of endothermic peaks lying in a region of 180–235 °C depend on the degree of substitution of Na^+ cations by Zn^{2+} in zeolite. The weight loss (Δm) of zeolites in the temperature interval from 20 to 500 °C is 21.0–26.1% (Table 3).

Table 2. Water content of the zeolite components in the Zn-containing systems after calcination (2 h, 500 °C) and saturation with water vapor at 20 °C*

Sample**	Composition (wt.%)	Water content (g of H_2O) (g of zeolite) $^{-1}$	Decrease in water content (rel.%)
$\text{Zn}(\text{NO}_3)_2/\text{NaY}$ (500)	19% ZnO + 100% NaY	0.259	18.8
$\text{Zn}(\text{NO}_3)_2/\text{NaY}$ (NH_3 , 500)	19% ZnO + 100% NaY	0.238	25.4
$\text{Zn}(\text{NO}_3)_2/\text{NaX}$ (500)	19% ZnO + 100% NaX	0.245	23.4
$\text{Zn}(\text{NO}_3)_2/\text{NaX}$ (NH_3 , 500)	19% ZnO + 100% NaX	0.256	20.0
$\text{Zn}(\text{NO}_3)_2/\text{NaA}$ (500)	19% ZnO + 100% NaA	0.184	30.8
$\text{Zn}(\text{NO}_3)_2/\text{NaA}$ (NH_3 , 500)	19% ZnO + 100% NaA	0.199	25.2
$\text{NaNO}_3/\text{ZnNaY}$ (500)	13.4% ZnO + 100% NaY	0.282	11.6
$\text{NaNO}_3/\text{ZnNaX}$ (500)	18.2% ZnO + 100% NaX	0.255	20.3
$\text{Zn}(\text{NO}_3)_2/\text{ZnNaY}$ (NH_3 , 500)	19% ZnO + 100% ZnNaY	0.266	22.7
$\text{Zn}(\text{NO}_3)_2/\text{ZnNaX}$ (NH_3 , 500)	19% ZnO + 100% ZnNaX	0.298	16.3

* According to the thermogravimetric data obtained in the 20–500 °C temperature interval.

** The temperature of the last treatment is given in parentheses after the name of the sample, and the NH_3 formula is presented if the system is prepared from an ammonia solution.

Table 3. Water content in the cationic zeolite forms according to the thermogravimetric data

Sample	Crystallochemical formula	Weight loss (wt.%)		Content of H_2O	
		20–500 °C	500–1000 °C	/g (g of zeolite) $^{-1}$	/molecules per unit cell
NaY	$\text{Na}_{60}\text{Al}_{60}\text{Si}_{132}\text{O}_{384}$	24.1	0.1	0.31	204
NaX	$\text{Na}_{85}\text{Al}_{85}\text{Si}_{107}\text{O}_{384}$	24.2	0.1	0.32	238
NaA	$\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{24}$	21.0	0.2	0.27	19.3
ZnNaY	$\text{Zn}_{21}\text{Na}_{18}\text{Al}_{60}\text{Si}_{132}\text{O}_{384}$	25.5	0.3	0.34	238
ZnNaX	$\text{Zn}_{30}\text{Na}_{25}\text{Al}_{85}\text{Si}_{107}\text{O}_{384}$	26.1	0.5	0.36	270

In the high-temperature region (500–1000 °C) corresponding to dehydroxylation,⁶ Δm does not exceed 0.5%. The data on zeolite dehydration agree with the water content in zeolites determined by adsorption methods⁶ (see Table 3). These data show that the content of adsorbed water reflects the free volume in the zeolite cavities, which is accessible for the sorbed and occluded molecules. It can be seen that the substitution of 70% of the Na^+ cations by Zn^{2+} in the samples with the faujasite structure results in the appearance of ~30 additional water molecules per unit cell, which is related to a decrease in the total number of cations.⁶ Note that the high-temperature weight loss (in the 500–1000 °C interval) corresponds to the removal of at most one H_2O molecule per unit cell, indicating a low thermal stability of the hydroxyl coverage of the Zn-substituted samples.

The thermogram of the starting $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ salt (Fig. 1, curve 1) shows that its decomposition to ZnO is complete at 330 °C following melting of the sample (an endothermic peak at 42 °C), water is removed accompanied by the partial hydrolysis of zinc nitrate and liberation of HNO_3 (100–330 °C). At temperatures higher than 200 °C, the gaseous products contain nitrogen oxides (NO_2 , NO , N_2O) and O_2 , indicating thermolysis of the nitrate anions.⁸

Unlike $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, sodium nitrate exhibits a higher stability: no weight loss of the sample is detected up to 590 °C (see Fig. 1, curve 2). The endothermic peak with a minimum at ~310 °C is caused by salt melting. Considerable weight losses are observed in the 600–950 °C interval ($\Delta m = 90.1\%$). Several endothermic peaks in this temperature region indicate a complicated character of NaNO_3 decomposition, which includes the formation of NaNO_2 with oxygen evolution,⁹ thermolysis of the nitrite anions, and sublimation of Na_2O . The removal of Na_2O from the sample is indicated by the Δm value, which exceeds the weight loss expected for the decomposition of NaNO_3 to Na_2O (Table 4).

The intervals of zinc nitrate melting and removal of H_2O and HNO_3 cannot be separated upon heat treatment of a $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + 2 \text{NaNO}_3$ mechanical mixture (see Fig. 1, curve 3), because the shape of the low-temperature endotherm in the thermogram is not fairly distinct. In addition, the TG curve of the mixture does not

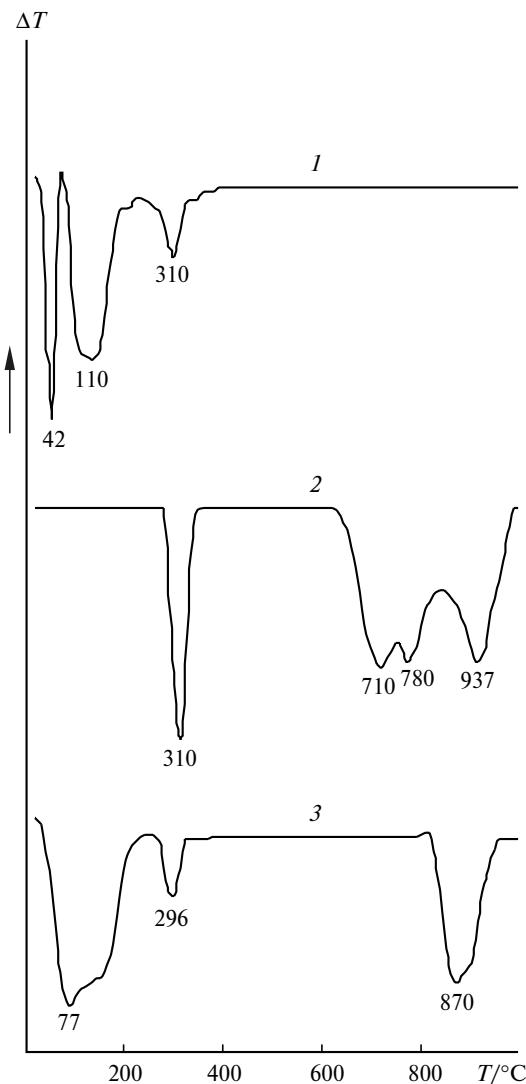


Fig. 1. Thermograms obtained by the DTA method for the individual salts $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1) and NaNO_3 (2) and their mixture $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + 2 \text{NaNO}_3$ (3).

represent a simple summation of the TG curves of the starting salts. The mixture is characterized by a considerable extension of the temperature region of the first step of NO_3^- anion decomposition (to 460 °C). The increase in stability of these anions is evidently caused by the in-

Table 4. Thermogravimetric data for the starting components and related systems

Sample*	Weight loss (wt.%)		Content (wt.%)		$\Delta_{\text{NO}_3^-}$ (rel.%)**
	20–500 °C	500–1000 °C	H_2O (or $\text{NH}_3 + \text{H}_2\text{O}$)	NO_3^-	
$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	72.5	0.1	36.3	36.3	0
NaNO_3	0	90.1	0	63.5	100
$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + 2 \text{NaNO}_3$	27.9	51.2	—	—	—
$\text{Zn}(\text{NO}_3)_2/\text{NaY}$ (100)	29.0	3.7	18.4	14.3	25.8
$\text{Zn}(\text{NO}_3)_2/\text{NaY}$ (500)	17.5	2.2	17.5	2.2	12.9
$\text{Zn}(\text{NO}_3)_2/\text{NaY}$ (NH_3 , 100)	25.0	3.6	13.4	15.2	23.7
$\text{Zn}(\text{NO}_3)_2/\text{NaY}$ (NH_3 , 500)	16.5	1.0	16.5	1.0	5.7
$\text{Zn}(\text{NO}_3)_2/\text{NaX}$ (100)	23.9	7.8	17.2	14.5	53.7
$\text{Zn}(\text{NO}_3)_2/\text{NaX}$ (500)	16.4	4.1	16.4	4.1	24.2
$\text{Zn}(\text{NO}_3)_2/\text{NaX}$ (NH_3 , 100)	22.5	6.7	14.2	15.1	44.5
$\text{Zn}(\text{NO}_3)_2/\text{NaX}$ (NH_3 , 500)	17.1	3.5	17.1	3.5	20.7
$\text{Zn}(\text{NO}_3)_2/\text{NaA}$ (100)	19.1	10.4	14.5	15.0	69.3
$\text{Zn}(\text{NO}_3)_2/\text{NaA}$ (500)	12.7	6.1	12.7	6.1	35.3
$\text{Zn}(\text{NO}_3)_2/\text{NaA}$ (NH_3 , 100)	22.7	8.8	16.9	14.6	60.4
$\text{Zn}(\text{NO}_3)_2/\text{NaA}$ (NH_3 , 500)	13.7	4.3	13.7	4.3	24.6
$\text{NaNO}_3/\text{ZnNaY}$ (100)	28.0	3.9	21.3	10.6	36.8
$\text{NaNO}_3/\text{ZnNaY}$ (500)	19.6	1.6	19.6	1.6	13.1
$\text{NaNO}_3/\text{ZnNaX}$ (100)	25.3	7.7	19.6	13.6	56.5
$\text{NaNO}_3/\text{ZnNaX}$ (500)	17.0	4.1	17.0	4.1	25.6
$\text{Zn}(\text{NO}_3)_2/\text{ZnNaY}$ (100)	34.2	1.2	21.7	13.7	8.7
$\text{Zn}(\text{NO}_3)_2/\text{ZnNaY}$ (NH_3 , 100)	33.7	0.7	20.4	14.0	5.0
$\text{Zn}(\text{NO}_3)_2/\text{ZnNaY}$ (NH_3 , 500)	18.2	0.3	18.2	0.3	1.7
$\text{Zn}(\text{NO}_3)_2/\text{ZnNaX}$ (100)	33.9	1.1	21.2	13.8	8.0
$\text{Zn}(\text{NO}_3)_2/\text{ZnNaX}$ (NH_3 , 100)	34.5	0.9	21.8	13.7	6.5
$\text{Zn}(\text{NO}_3)_2/\text{ZnNaX}$ (NH_3 , 500)	19.7	0.6	19.7	0.6	3.5

* The temperature of the last treatment is given in parentheses after the name of the sample, and the NH_3 formula is presented if the system is prepared from an ammonia solution.

** Relative decrease in the initial weight of the NO_3^- ions at temperatures above 500 °C.

fluence of the Na^+ cations. In the 460–600 °C interval, for the mixture consisting mainly of ZnO and NaNO_3 no loss in weight is observed. At temperatures >600 °C the presence of ZnO noticeably changes the character of NaNO_3 decomposition as indicated by the absence of endotherms at 600–800 °C in the thermograms, which are characteristic of NaNO_3 .

Thus, the results obtained for the individual zeolites and salts, as well as for the $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + 2 \text{NaNO}_3$ mixture, make it possible to distinguish two main temperature regions in which the weight loss occurs. In the 20–500 °C interval, absorbed water and water of crystallization are removed, and the portion of the NO_3^- anions is decomposed that predominantly interacts with the Zn^{2+} cations. In the second temperature region (500–1000 °C), a decrease in the weight is mainly caused by the decomposition of NaNO_3 and products of its partial transformation.

According to the previous studies,⁶ zeolites interact actively with inorganic salts to form occlusion compounds. The latter occupy a considerable volume of the intracrystalline space. Therefore, the content of water adsorbed

in zeolites can be a reliable measure of the extension of zeolite interaction with zinc and sodium nitrate.

In order to prove such an interaction, we can compare the water content in the real mixture of zeolite with $\text{Zn}(\text{NO}_3)_2$ and in a hypothetical composition in which the salt–zeolite interaction is absent. Below we present the Δm values calculated for the real ($\text{Zn}(\text{NO}_3)_2/\text{NaY}$ (100)*) and hypothetical ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + \text{NaY}$) mixtures; Δm for the latter were calculated from the parameters of the starting components.

Sample	Δm (wt.%) (20–500 °C)	Content of H_2O (wt.%)
$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + \text{NaY}$	40.8	28.4
$\text{Zn}(\text{NO}_3)_2/\text{NaY}$ (100)	29.0	18.4

The different concentrations of H_2O in these systems are related to the interaction of components in $\text{Zn}(\text{NO}_3)_2/\text{NaY}$ (100). On the one hand, ion exchange

* Hereafter the numbers in parentheses after the name of the sample designate the temperature of its last treatment.

that occurs when NaY is impregnated with a solution of $\text{Zn}(\text{NO}_3)_2$ produces NaNO_3 , which does not form crystal hydrates. On the other hand, occluded ions can be localized in zeolite pores to decrease the free volume of pores, which determined the water contents of zeolites.

The assumption about the involvement of an ion exchange agrees with the shape of the thermograms for the $\text{Zn}(\text{NO}_3)_2/\text{NaY}$ (100) system (Fig. 2, curve 1). The first step of weight loss lies in the temperature region of 50–330 °C and is probably caused by the loss of H_2O and HNO_3 accompanied by a partial decomposition of the acid. A change in the nature of sorption sites is indicated by a shift of the low-temperature minimum in the DTA curve as large as 105 °C when compared to the position of the peak of the initial components. The further weight loss continues up to 750 °C. The endotherm corresponding to the initial step of this process has a maximum at

490 °C. Such a high temperature indicates that this thermal effect is mainly caused by the decomposition of the NO_3^- ions, whose stabilization involves the Na^+ cations. The Δm value at $T > 500$ °C is 25.8% of the initial weight of the nitrate anions (see Table 4). The thermal stability of the NO_3^- anions in the $\text{Zn}(\text{NO}_3)_2/\text{NaY}$ (100) system is intermediate between those for zinc and sodium nitrates.

Calcination of the $\text{Zn}(\text{NO}_3)_2/\text{NaY}$ (100) sample for 2 h at 500 °C followed by its saturation with water vapor produces a system, which desorbs water in the low-temperature region in a similar way with the starting NaY zeolite (see Fig. 2, curve 2). In contrast to zeolite NaY , the $\text{Zn}(\text{NO}_3)_2/\text{NaY}$ (500) system shows the weight loss in the 500–750 °C interval, which indicates the decomposition of the NO_3^- anions (and/or products of their transformations). Thus, after the thermal pre-treatment of the

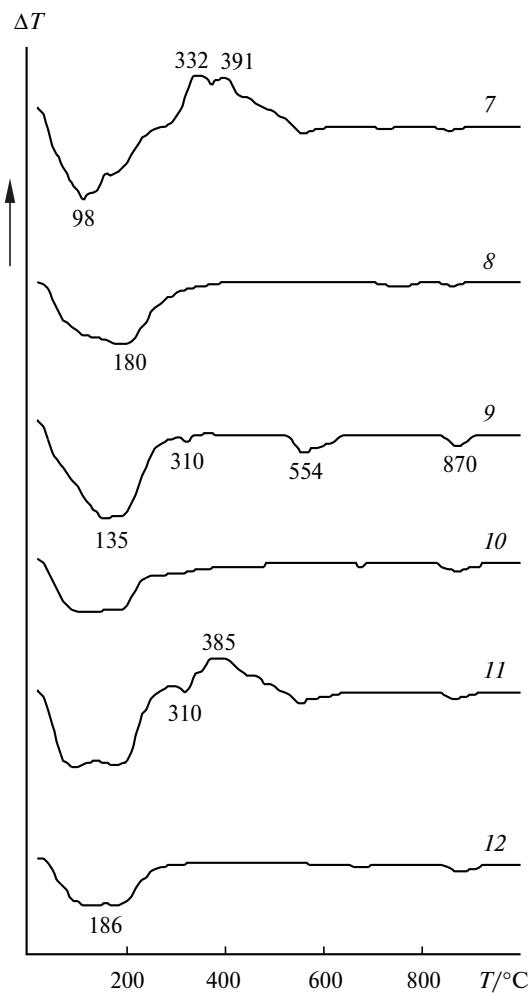
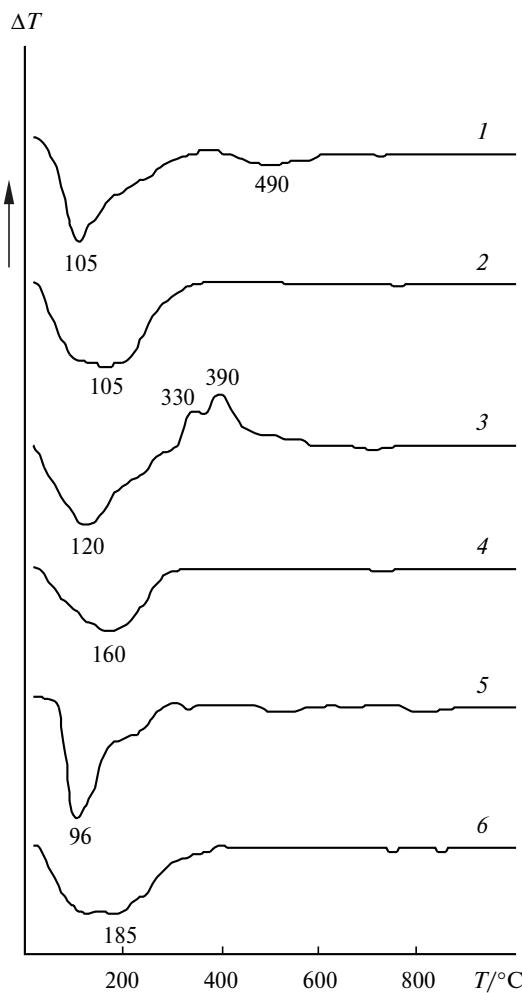


Fig. 2. Thermograms obtained by the DTA method for the systems of the $\text{Zn}(\text{NO}_3)_2/\text{NaZ}$ type: $\text{Zn}(\text{NO}_3)_2/\text{NaY}$ (100) (1), $\text{Zn}(\text{NO}_3)_2/\text{NaY}$ (500) (2), $\text{Zn}(\text{NO}_3)_2/\text{NaY}(\text{NH}_3, 100)$ (3), $\text{Zn}(\text{NO}_3)_2/\text{NaY}(\text{NH}_3, 500)$ (4), $\text{Zn}(\text{NO}_3)_2/\text{NaX}$ (100) (5), $\text{Zn}(\text{NO}_3)_2/\text{NaX}$ (500) (6), $\text{Zn}(\text{NO}_3)_2/\text{NaX}(\text{NH}_3, 100)$ (7), $\text{Zn}(\text{NO}_3)_2/\text{NaX}(\text{NH}_3, 500)$ (8), $\text{Zn}(\text{NO}_3)_2/\text{NaA}$ (100) (9), $\text{Zn}(\text{NO}_3)_2/\text{NaA}$ (500) (10), $\text{Zn}(\text{NO}_3)_2/\text{NaA}(\text{NH}_3, 100)$ (11), and $\text{Zn}(\text{NO}_3)_2/\text{NaA}(\text{NH}_3, 500)$ (12).

$\text{Zn}(\text{NO}_3)_2/\text{NaY}$ system at 500 °C, it retains some amount (12.9% of the initial weight of the NO_3^- ions) of the NO_x particles (see Table 4).

The use of an aqueous-ammonia solution of zinc nitrate for zeolite impregnation significantly changes the thermal properties of the systems formed. This is well seen by comparison of the thermograms of the $\text{Zn}(\text{NO}_3)_2/\text{NaY}$ (100) and $\text{Zn}(\text{NO}_3)_2/\text{NaY}$ (NH_3 , 100)* samples (see Fig. 2, curves 1 and 3). Curve 3 shows a maximum at 330 °C with the second exotherm (~390 °C) followed by the endothermic peaks at 700–800 °C. The exothermic effects observed upon heat treatment of the $\text{Zn}(\text{NO}_3)_2/\text{NaY}$ (NH_3 , 100) system indicate the intra-zeolite oxidation of the NH_3 molecules,¹⁰ which are probably coordinated with the Zn^{2+} cations and fragments of the zeolite structure.

Both air oxygen and NO_3^- anions that are present in the system can be involved in the oxidation of the NH_3 molecules (or the NH_4^+ cations) retained in $\text{Zn}(\text{NO}_3)_2/\text{NaY}$ (NH_3 , 100). The fraction of anions remained in this sample at temperatures >500 °C is 24% of their initial content (see Table 4). In the case of $\text{Zn}(\text{NO}_3)_2/\text{NaY}$ (100), Δm at 500–1000 °C is equal to 26%, which indicates that the NO_3^- anions can be reduced by NH_3 (or NH_4^+). The data obtained for the $\text{Zn}(\text{NO}_3)_2/\text{NaY}$ (NH_3 , 500) system show that NO_3^- is removed more rapidly under the conditions of thermal pre-treatment: the Δm value in the 500–1000 °C interval is halved compared to that for the $\text{Zn}(\text{NO}_3)_2/\text{NaY}$ (500) sample.

Thus, ion exchange occurs at the step of preparation of the sample zeolite NaY-based systems, and NH_3 is involved in the removal of the nitrate anions. These regularities remain valid for the samples based on NaX zeolite. The low-temperature endotherm observed on heat treatment of $\text{Zn}(\text{NO}_3)_2/\text{NaX}$ (100) (see Fig. 2, curve 5) is more narrow than that of the starting zeolite and has a distinct minimum at 96 °C. The shift of desorption processes to the low-temperature region indicates that the interaction of H_2O with zeolite is weakened due to its modification with zinc nitrate. The content of H_2O also decreases: it is ~60% of the H_2O amount in the hypothetical $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + \text{NaX}$ system, whose components are assumed to be non-interacting. Such a decrease can be a consequence of ion exchange and filling of the zeolite cavities with occluded ions in the real $\text{Zn}(\text{NO}_3)_2/\text{NaX}$ (100) system. The interaction of the zeolite Na^+ cations with the salt anions is indicated by an extension of the temperature interval (to 850 °C) of the weight loss for this sample. At $T > 500$ °C, the NO_3^- loss more than twofold exceeds the weight loss, which is de-

termined for the analogous system based on zeolite NaY (see Table 4). The differences observed for the stability of the nitrate anions are evidently related to the fact that the $\text{Na}^+/\text{NO}_3^-$ molar ratio is 1.0 and 1.36 for the $\text{Zn}(\text{NO}_3)_2/\text{NaY}$ (100) and $\text{Zn}(\text{NO}_3)_2/\text{NaX}$ (100) systems, respectively. In other words, the higher content of Na_2O in zeolite NaX (than that in NaY) increases the fraction of the NO_3^- anions, which interact with the Na^+ cations.

The $\text{Zn}(\text{NO}_3)_2/\text{NaX}$ (500) sample treated at a high temperature retains 24.2% of the initial weight of NO_3^- (see Table 4, Fig. 2, curve 6), which is twofold greater than that in $\text{Zn}(\text{NO}_3)_2/\text{NaY}$ (500). On preparing the zeolite NaX-based system (see Fig. 2, curve 7) replacement of an aqueous solution of zinc nitrate by an aqueous-ammonia solution induces the same changes that were observed for the systems obtained from NaY (see Fig. 2, curve 3). For example, under the conditions of temperature-programmed heating of the $\text{Zn}(\text{NO}_3)_2/\text{NaX}$ (NH_3 , 100) sample, NH_3 is oxidized in an interval of 290–430 °C. As in the case of $\text{Zn}(\text{NO}_3)_2/\text{NaY}$ (NH_3 , 100), oxidation occurs in two steps (exotherms at 331 and 391 °C). Coincidence of these temperatures for the systems based on NaY and NaX can indicate that the sites interacting with NH_3 in these samples are similar. In the region of high temperatures (500–1000 °C) for $\text{Zn}(\text{NO}_3)_2/\text{NaX}$ (NH_3 , 100), almost a half of the starting NO_3^- amount is decomposed (see Table 4). After the treatment for 2 h at 500 °C, this system retains more than 20% of the nitrate anions (see Table 4). Their decomposition in the 600–900 °C interval, as in the case of the $\text{Zn}(\text{NO}_3)_2/\text{NaX}$ (500) sample, occurs in two steps as indicated by the shape of the DTA curve (see Fig. 2, curve 8).

The systems based on zeolite NaA differ noticeably from the faujasite samples. For example, $\text{Zn}(\text{NO}_3)_2/\text{NaA}$ (100) is dehydrated in a wider temperature interval (see Fig. 2, curve 9). This system has lower H_2O content (14.5%) than similar samples based on zeolites Y and X containing 18.4 and 17.2% of H_2O , respectively (see Table 4). These differences can be attributed to the higher ion-exchange capacity and to an enhanced amount of NaNO_3 that formed. A small size of cavities in the structure of zeolite A should also be taken into account, because this can decrease the amount of adsorbed water in the presence of guest salts. The relative decrease in the H_2O content on going from a hypothetical $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + \text{NaA}$ mixture to the $\text{Zn}(\text{NO}_3)_2/\text{NaA}$ (100) sample reaches 45%. Assuming that an ion exchange occurring on preparing the real mixture reaches an extent of 100%, the system formed could have the following composition: 27.5 wt.% NaNO_3 + 72.5 wt.% 0.66 ZnNaA (dry basis). If the water content of the zeolite component (21%) is retained, the H_2O content in this system should be 16.2%, which is higher than the value determined for $\text{Zn}(\text{NO}_3)_2/\text{NaA}$ (100) (see Table 4,

* The NH_3 formula in parentheses after the name of the sample indicates that the system was prepared by impregnation with an aqueous-ammonia solution of $\text{Zn}(\text{NO}_3)_2$.

14.5%). This indicates that some portion of the salt is trapped in the zeolite cavities along with displacement of H_2O .

The weight loss of the $\text{Zn}(\text{NO}_3)_2/\text{NaA}$ (100) sample in the high-temperature region occurs in two steps: at 500–600 and 800–870 °C. The total Δm value at 500–1000 °C is 10.4 wt.% (or 69.3% of the starting weight of NO_3^-) (see Table 4). This parameter is maximum for the studied $\text{Zn}(\text{NO}_3)_2/\text{NaZ}$ systems, which is evidently related to the high $\text{Na}^+/\text{NO}_3^-$ molar ratio (1.5) in the NaA-based sample. The DTA curve (see Fig. 2, curve 9) contains the endothermic peak at ~310 °C, indicating that $\text{Zn}(\text{NO}_3)_2/\text{NaA}$ contains a significant amount of NaNO_3 , which melts at this temperature (see Fig. 1, curve 2). After the 2-h treatment at 500 °C, the NaNO_3 phase in the $\text{Zn}(\text{NO}_3)_2/\text{NaA}$ (500) sample is absent (no endotherm at 310 °C is observed), although the weight loss is significant (6.1%) in the temperature interval from 500 to 900 °C (see Fig. 2, curve 10). This indicates occlusion of 35.3% of the nitrate anions in $\text{Zn}(\text{NO}_3)_2/\text{NaA}$ (500) (see Table 4).

The use of an aqueous-ammonia solution of zinc nitrate for impregnation of powdered NaA produces the $\text{Zn}(\text{NO}_3)_2/\text{NaA}$ (NH_3 , 100) sample, which exhibits both NaNO_3 melting (the endotherm at 310 °C) and NH_3 oxidation (the exotherm at 330–380 °C) (see Fig. 2, curve 11). The presence of NH_3 decreases Δm at 500–1000 °C compared to the weight loss for the system prepared from an aqueous solution (see Table 4), indicating the involvement of the NH_3 molecules in the reduction of the NO_3^- anions. However, a significant portion of the anions (60%) is retained in $\text{Zn}(\text{NO}_3)_2/\text{NaA}$ (NH_3 , 100) at $T > 500$ °C, which additionally confirms the stabilizing influence of the Na^+ cations in the systems under study.

The thermograms of the systems prepared by impregnation of ion-exchange zeolites ZnNaY and ZnNaX with a solution of NaNO_3 are presented in Fig. 3. The thermograms of the $\text{NaNO}_3/\text{ZnNaY}$ (100) and $\text{NaNO}_3/\text{ZnNaY}$ (500) samples (see Fig. 3, curves 1 and 2) are close in shape to the thermograms of the $\text{Zn}(\text{NO}_3)_2/\text{NaY}$ systems (see Fig. 2, curves 1 and 2). In fact, the endotherm caused by the dehydration of $\text{NaNO}_3/\text{ZnNaY}$ (100) has a distinct maximum at 100 °C. However, on going to $\text{NaNO}_3/\text{ZnNaY}$ (500), the DTA curve in this region becomes smoother, and the maximum shifts toward 150 °C. These changes can be explained as follows. At the step of ZnNaY impregnation with an solution of NaNO_3 accompanied by ion exchange, crystal hydrates of zinc nitrate are formed, and their dehydration occurs in the low-temperature region. When the system is treated at 500 °C, zinc nitrate decomposes, and the main part of H_2O interacts with zeolite, which increases the temperature of desorption.

The interaction of the Zn^{2+} and NO_3^- ions in the $\text{NaNO}_3/\text{ZnNaY}$ (100) system is indicated by the fact that two thirds of the nitrate anions are decomposed at $T < 500$ °C under the conditions of thermal analysis (see Table 4). The pretreatment for 2 h at 500 °C leads to a greater loss of NO_3^- . It cannot be excluded that the difference in the properties of $\text{NaNO}_3/\text{ZnNaY}$ (100) and $\text{Zn}(\text{NO}_3)_2/\text{NaY}$ (100) is caused by the chosen conditions of preparation when the ion exchange does not reach equilibrium and, hence, the ratios of NO_3^- ions interacting with the Na^+ and Zn^{2+} cations are different for these systems. It should also be taken into account that the ZnO content in $\text{Zn}(\text{NO}_3)_2/\text{NaY}$ is higher than that in $\text{NaNO}_3/\text{ZnNaY}$ (see Table 1). This can be another reason for the slower decomposition of NO_3^- in the ZnNaY-based system.

The $\text{NaNO}_3/\text{ZnNaX}$ and $\text{Zn}(\text{NO}_3)_2/\text{NaX}$ systems have almost the same composition (see Table 1), and their thermal properties are virtually the same (see Table 4, Fig. 2, curves 5 and 6, Fig. 3, curves 3 and 4). This indicates that different methods of preparation (impregnation of NaX with a solution of $\text{Zn}(\text{NO}_3)_2$ or impregnation of ion-exchange zeolite ZnNaX with a solution of NaNO_3) produce the systems with the same distribution of the cations and NO_3^- ions due to the high mobility of occluded salts in the zeolite cavities.

Another method used for preparation of the non-acidic zeolite systems with a high content of ZnO is impregnation of ion-exchange zinc forms with $\text{Zn}(\text{NO}_3)_2$ following by the decomposition of zinc nitrate. Curve 5 in Fig. 3 shows that the $\text{Zn}(\text{NO}_3)_2/\text{ZnNaY}$ (100) sample contains the $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ crystal hydrate, whose melting at 43 °C results in heat absorption. This sample dehydrates especially rapidly in the 80–180 °C region (the endotherm with a maximum at 125 °C). The further decrease in the weight and endothermic effects (a shoulder at ~220 °C and an extreme at 380 °C) indicate that the almost complete removal of H_2O and decomposition of the NO_3^- ions are reached at 500 °C. According to the H_2O content (22%), some zeolite cavities are filled with occluded ions, because the calculated amount of H_2O in the hypothetical $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + \text{NaY}$ mixture is much higher than that found in the experiment. A small portion of the NO_3^- anions remained in the sample (8.7%) at the temperature > 500 °C is evidently related to a low Na_2O content in this sample (<4 mol.% (see Table 1)).

Low stability of the nitrate anions in the systems of this type is also confirmed by the data obtained for the non-calcined sample prepared by the impregnation of zeolite ZnNaY with an aqueous-ammonia solution of zinc nitrate (see Fig. 3, curve 6). The presence of the NH_3 molecules noticeably changes the shape of the DTA curve in the low-temperature region (below 300 °C) and results in the appearance of a broad exotherm in the 320–400 °C

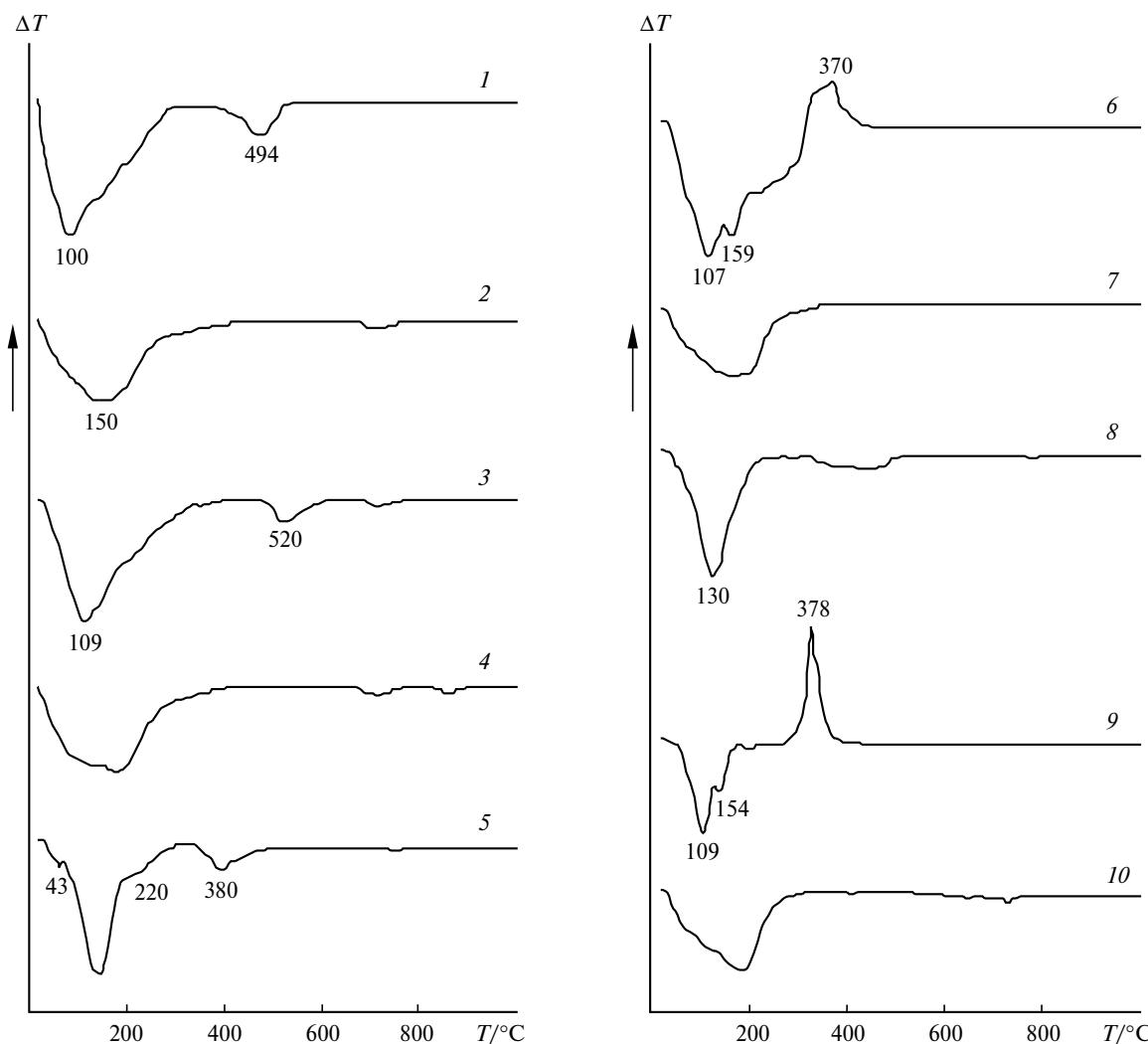


Fig. 3. Thermograms obtained by the DTA method for the systems of the $\text{NaNO}_3/\text{ZnNaZ}$ and $\text{Zn}(\text{NO}_3)_2/\text{ZnNaZ}$ types: $\text{NaNO}_3/\text{ZnNaY}$ (100) (1), $\text{NaNO}_3/\text{ZnNaY}$ (500) (2), $\text{NaNO}_3/\text{ZnNaX}$ (100) (3), $\text{NaNO}_3/\text{ZnNaX}$ (500) (4), $\text{Zn}(\text{NO}_3)_2/\text{ZnNaY}$ (100) (5), $\text{Zn}(\text{NO}_3)_2/\text{ZnNaY}$ (NH_3 , 100) (6), $\text{Zn}(\text{NO}_3)_2/\text{ZnNaY}$ (NH_3 , 500) (7), $\text{Zn}(\text{NO}_3)_2/\text{ZnNaX}$ (100) (8), $\text{Zn}(\text{NO}_3)_2/\text{ZnNaX}$ (NH_3 , 100) (9), and $\text{Zn}(\text{NO}_3)_2/\text{ZnNaX}$ (NH_3 , 500) (10).

interval. As in the case of other systems, NH_3 oxidation favors the removal of 95% of the NO_3^- ions below 500 °C. After the treatment at 500 °C, almost all NO_3^- ions are removed from the zeolite.

The specific features of the behavior of the zeolite ZnNaY -based systems are also found for the $\text{Zn}(\text{NO}_3)_2/\text{ZnNaX}$ samples (see Table 4, Fig. 3, curves 8–10). The DTA data show that $\text{Zn}(\text{NO}_3)_2/\text{ZnNaX}$ (100) contains zinc nitrate crystal hydrates (the endotherm at 43 °C). The presence of the crystal hydrate shifts the dehydration interval in the low-temperature region (the maximum of heat absorption lies at ~130 °C). A decreased water content of the system (21%) compared to the H_2O content in the hypothetical $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + \text{ZnNaX}$ mixture (30%) indicates that some NO_3^- ions are trapped

in the zeolite cavities. The main fraction of NO_3^- ions (92.0%) is decomposed at temperatures below 500 °C (see Table 4). In the presence of NH_3 , this process is accelerated thus increasing the degree of decomposition of the nitrate anions to 93.5% ($\text{Zn}(\text{NO}_3)_2/\text{ZnNaX}$ (NH_3 , 100) sample). Only 3.5% of the NO_3^- anions are retained after the preliminary thermal treatment ($\text{Zn}(\text{NO}_3)_2/\text{ZnNaX}$ (NH_3 , 500) sample).

The thermogravimetric results for several systems, which were not treated at 500 °C, are presented in Fig. 4. It is seen that with an increase in the Na_2O content in the systems the process of NO_3^- removal shifts toward high temperatures. For the $\text{Zn}(\text{NO}_3)_2/\text{ZnNaY}$ (100) sample with a low content of Na_2O , loss in weight of NO_3^- exceeds 50% on heating to 400 °C. The highest stability of

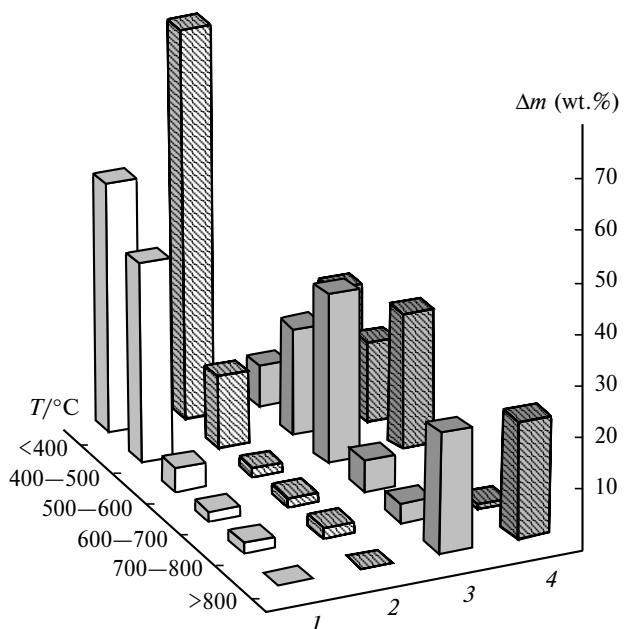


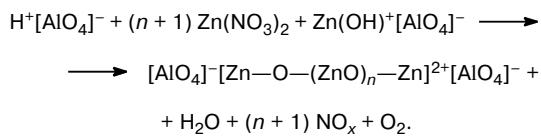
Fig. 4. Diagram of the dependence of the thermostability of the NO_3^- ions on the composition and method of preparation of the zeolite systems: $\text{Zn}(\text{NO}_3)_2/\text{ZnNaY}$ (100) (1), $\text{Zn}(\text{NO}_3)_2/\text{ZnNaY}(\text{NH}_3, 100)$ (2), $\text{Zn}(\text{NO}_3)_2/\text{NaA}$ (100) (3), and $\text{Zn}(\text{NO}_3)_2/\text{NaA}(\text{NH}_3, 100)$ (4) (Δm is the weight loss of the corresponding sample).

the nitrate anions is observed for the NaA-based systems (21.4% Na_2O). Even at $T > 800^\circ\text{C}$, they retain more than 20% of the initial weight of NO_3^- .

Another factor determining the rate of NO_3^- removal is the presence of NH_3 in the systems (see Fig. 4). For the most part of the samples prepared from aqueous-ammonia solutions, the fraction of the nitrate anions removed below 400°C increases considerably (~2-fold). This is related to the involvement of the NH_3 molecules (or NH_4^+ ions) in the reduction of the NO_3^- ions. A possible removal of the nitrate ions from the KNO_3/NaY zeolite systems is indicated by the IR spectroscopic data¹¹ which monitor a decrease in the concentration of the NO_3^- ions on contact with vapors of oxygen-containing organic compounds under the catalytic conditions at 500°C . The use of NH_3 as a reducing agent favors the removal of the NO_3^- ions.

The thermal transformations of the systems under study include ZnO formation due to the decomposition of the nitrate anions. All systems are characterized by a decrease in the content of adsorbed water (see Table 2). This can be explained by the arrangement of a portion of zinc oxide inside the zeolite cavities as supported by the data on the catalytic properties of the zeolite systems in methanol transformation.^{4,5} The starting zeolites, including the Na forms,⁵ are highly active in the dehydration of MeOH to form dimethyl ether, indicating that they contain acidic sites. After the zeolites were modified with Zn and Na

nitrates, their dehydrating activity decreased sharply, and the selectivity with respect to the products of MeOH dehydrogenation (CH_2O , CO) increased simultaneously. The neutralization of the acidic sites formed in the ion-exchange ZnNaZ zeolites due to the heterolytic decomposition of the H_2O molecules can be presented by the following scheme:



The existence of similar bridging groups has also been reported in the study of the zeolite—oxide systems.^{12,13}

It is assumed that the $[\text{Zn}—\text{O}—(\text{ZnO})_n—\text{Zn}]^{2+}$ oxide-ionic species, which are localized in the zeolite cavities, have such a size that allows the charges of the isolated $[\text{AlO}_4]^-$ tetrahedra to be compensated without H_2O involvement. At the same time, it cannot be excluded for the samples under study that some Al^{3+} cations leave the zeolite structure under the condition of formation of the ZnO -containing systems, decreasing the concentration of the H^+ -acidic sites. As a result of partial zeolite decomposition, their water content decreases.

The water content of zeolite depends on the number of guest anions, which are retained in the zeolite pores. For example, for the $\text{Zn}(\text{NO}_3)_2/\text{NaA}$ (500) system containing the greatest amount of the NO_3^- ions among the pre-calcined samples, the relative decrease in the water content of the zeolite component is also the highest (see Table 2, 30.8%). The high-temperature treatment of NaNO_3/NaY is known¹⁴ to result in the penetration of salt into the zeolite structure, including small cavities with entrances smaller than the diameter of occluded ions. It is proposed that the NO_3^- anions are decomposed with oxygen loss to smaller particles (NO , NO_2), which are oxidized to NO_3^- again after penetration into the sodalite cavities. The intrazeolite localization of ions markedly enhances their thermal stability.¹⁴ Our data demonstrate this possibility for the zeolite systems containing ZnO . This is most evident for the zeolite NaA-based samples (see Table 4), which is related to the involvement of the Na^+ cations in NO_3^- stabilization. Individual sodium nitrate differs slightly in the character of decomposition from these zeolite systems. The weight loss of NaNO_3 occurs from 600°C (see Fig. 1, curve 2), whereas NO_x is removed from the $\text{Zn}(\text{NO}_3)_2/\text{NaA}$ samples mainly at $T > 800^\circ\text{C}$ (see Fig. 2, curves 9–12).

Thermal transformations in the zeolite systems containing zinc and sodium nitrates include, most likely, the following steps. When NaZ is impregnated with a solution of $\text{Zn}(\text{NO}_3)_2$ (or of ZnNaZ with a solution of NaNO_3) followed by drying at 100°C , ion exchange occurs along with partial filling of the zeolite cavities with ions to re-

duce the water content of the zeolite component. The cation redistribution between the salt and zeolite allows the NO_3^- ions to interact with both Zn^{2+} and Na^+ , which differ strongly in stabilizing effect on NO_3^- . As a result, the decomposition of the NO_3^- ion occurs in the temperature regions characteristic of transformations of zinc nitrate (<325 °C) and sodium nitrate (>600 °C) and also in the intermediate interval. The depth of removal of nitrate anions is influenced by the composition of the $\text{Na}-\text{Zn}$ systems, the method of their preparation, and conditions of pretreatment. In the ammonia systems, the NH_3 molecules (or NH_4^+ ions), whose content in the samples is fairly high even at 300–400 °C, are involved in this process.

References

1. I. E. Maxwell and W. H. J. Stork, *Stud. Surf. Sci. Catal.*, 2001, **137**, 747.
2. M. E. Davis, A. Katz, and W. R. Ahmad, *Chem. Mater.*, 1996, **8**, 1820.
3. N. Herron and D. L. Thorn, *Adv. Mater.*, 1998, **10**, 1173.
4. N. Ya. Usachev, E. P. Belanova, A. V. Kazakov, V. P. Kalinin, A. S. Fomin, I. M. Kruckovsky, G. V. Antoshin, and O. K. Atal'yan, *Stud. Surf. Sci. Catal.*, 2001, **135**, 206.
5. N. Ya. Usachev, E. P. Belanova, A. S. Fomin, I. M. Kruckovsky, S. A. Kanaev, and O. K. Atal'yan, *Neftekhimiya*, 2002, **42**, 95 [*Petroleum Chemistry*, 2002, **42**, 78 (Engl. Transl.)].
6. D. W. Breck, *Zeolite Molecular Sieves. Structure, Chemistry and Use*, J. Wiley and Sons, New York–London–Sydney–Toronto, 1974, 728 pp.
7. K. Sigrist and H. Stach, *Thermochim. Acta*, 1996, **278**, 145.
8. A. Malecki, R. Gajerski, S. Łabuś, B. Prochowska-Klisz, and K. T. Wojciechowski, *J. Therm. Anal. Calorim.*, 2000, **60**, 17.
9. E. S. Freeman, *J. Phys. Chem.*, 1956, **60**, 1487.
10. A. P. Bolton and M. A. Lanewala, *J. Catal.*, 1970, **18**, 154.
11. Y. Chun, J. H. Zhu, Y. Wang, D. K. Sun, and Q. H. Xu, *Proc. 12th Int. Zeolite Conf. (Baltimore, Maryland, July 5–10, 1998)*, Eds. M. M. J. Treacy, B. K. Marcus, M. E. Bisher, and J. B. Higgins, MRS, Warrendale (Pennsylvania), 1999, **2**, 989.
12. A. Seidel, F. Rittner, and B. Boddenberg, *J. Phys. Chem. B*, 1998, **102**, 7176.
13. A. L. Yakovlev, A. A. Shubin, G. M. Zhdomirov, and R. A. van Santen, *Catal. Lett.*, 2000, **70**, 175.
14. J. A. Rabo, in *Zeolite Chemistry and Catalysis (ACS Monograph 171)*, Ed. J. A. Rabo, ACS, Washington, DC, 1976, 332.

Received February 14, 2003;
in revised form July 10, 2003