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THERMAL PROPERTIES OF Y-TYPE ZEOLITES

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Abstract

The thermal and structural properties of two parent NaY zeolites and of those modified by ion exchange (ReNaY, HNaY, FeNaY) were investigated by simultaneous thermal analysis (TG-DTA-DTG) and by X-ray diffraction spectroscopy. Both the intracrystalline water and the zeolite framework were in our attention. The impurities (Fe) located in the lattice as well as the ions which entered by ion exchange (Re, H, Fe) influence the properties of the zeolites. The values of the activation energy of the dehydration process prove that the water molecules are more strongly bonded in all modified samples than in the parent ones. As compared to the NaY zeolites, an increased thermal stability, of about 100°C was revealed for ReNaY or of about 180°C for HNaY, and a decreased stability, of about 50°C, for FeNaY samples. The temperature at which the lattice break-down begins T_{amf}, estimated by following the X-ray diffraction patterns for samples heated in air at temperatures from 300 to 1100°C, is the temperature which may be related to the structural characteristics of the zeolites, i.e., to the lattice constant of the uncalcined materials. The XRD studies reveal the heterogeneity of the crystallites constituting the zeolite material from both the point of view of the lattice constant values and the thermal stability.

As the temperature T_{amf}, generally, does not coincide with the temperature of the first exothermic peak, T_1, of the DTA curve, we suggest the temperature T_{amf} to be taken as an unambiguous measure of the thermal stability.

Keywords: catalysts, NaY zeolites

Introduction

The X- and Y-type zeolites containing transition metal ions are extensively used as catalysts for petroleum cracking and hydrocarbon conversion reactions. For an industrial catalyst it is very important to exhibit outstanding thermal stability. As the thermal stability depends on the degree of cation exchange, on the

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type and valence of cations as well as on their distribution among cation sites, the properties of X and Y Linde- type zeolites modified by ion exchange with multivalent cations were investigated by electron paramagnetic resonance method in a number of our previous papers [1–4].

The aim of this work is to present some results concerning the influence of cation exchange with hydrogen, rare-earths and iron, respectively, on the structural and thermal properties of the Y-type zeolites prepared by ICITPR-Ploiesti.

Materials

The investigated Na-Y-type zeolites prepared according to OSIM patents [5, 6] using different silica sources, i.e., silicic acid for the sample NaY-1 and sodium silicate for the sample NaY-2, respectively, were supplied by ICITPR-Ploiesti, Romania. A series of modified zeolites (HNaY, ReNaY, FeNaY) was prepared by ion exchange. The hydrogen-containing one (HNaY) was obtained as follows: the NaY zeolite was first converted into the ammonium form by mixing it at 90°C with a solution containing 5%(wt.) NH_4Cl, and then, by calcining the filtered and washed suspension at 500°C it was subsequently reduced to the hydrogen form. The rare-earth exchanged zeolites were prepared by contacting the powder of NaY zeolite with 5%(wt) mixed rare-earth chloride ($ReCl_3$) solution. The iron-exchanged samples (FeNaY) were obtained by mixing at room temperature the NaY material with a solution containing 5%(wt.) $Fe(NO_3)_3$ and then stirring the mixture for 2 h at 90°C. Repeated cation exchanges were performed to obtain samples with the desired content of iron. Fi-

Table 1 Composition of the samples

Samples	SiO_2/Al_2O_3	Na_2O	MnO	Fe_2O_3	Re_2O_3	Ads. capacity /
	mol	%wt				g C_6H_6/100 g
NaY-1	5.10	9.68	0.003	0.10		25.0
ReNaY-1	5.07	3.40	0.028	0.20	13	19.6
HNaY-1	5.05	0.48	0.015	0.10		19.8
FeNaY-1	5.10	9.40	0.003	0.36		25.4
FeNaY-1	5.10	7.20	0.010	2.55		25.8
NaY-2	5.06	10.1	0.010	0.28		25.6
ReNaY-2	5.03	3.23	0.009	0.72	12.98	22.0
HNaY-2	5.04	0.41	0.005	0.27		20.3
FeNaY-2	5.06	9.80	0.009	0.54		26.0
FeNaY-2	5.06	7.36	0.021	3.00		26.2

nally, all suspensions were filtered, washed with distilled water and dried in air at 80°C. The chemical composition of the investigated samples, found by atomic absorption spectroscopy, is presented in Table 1. Note than iron and manganese are always present in trace amount in the parent zeolites, the content of undesired impurities being lower in the NaY-1 type than in the NaY-2.

Thermal analysis

The thermal methods of analysis are very useful in the investigation of the intracrystalline water properties as well as in the separation and identification of different structural changes of the zeolite framework. The DTA, TG and DTG curves were obtained by using a Paulik type derivatograph, by running the samples in air with a constant heating rate of 10 deg·min^{-1} to a maximum temperature of 1100°C. The DTA curve in Fig. 1 is characterized by a sharp and strong endothermic peak and two exothermic ones. The first peak, $T_{peak} \approx 220°C$, with a base width of ΔT, given in Table 2, is due to the loss of water molecules from zeolite cavities, the process being also visible in both the TG and DTG curves.

Table 2 Thermal analysis results

	Weight	DTA				E /
Samples	loss / %	Endothermic peak	Base width	Exothermic peak		kJ·mol^{-1}
	(from TG)	T / °C	ΔT / °C	T_1 / °C	T_2 / °C	
NaY-1	26.0	230	70–440	930	–	18.66
ReNaY-1	23.8	220	70–430	980	–	22.70
HNaY-1	14.2	195	100–350	1020	–	25.80
FeNaY-1	26.0	230	40–480	950	1050	21.93
FeNaY-1	24	220	60–480	920	1060	30.74
NaY-2	26.4	230	60–400	830	920	18.70
ReNaY-2	24.3	220	60–400	960	–	23.90
HNaY-2	13.0	190	100–370	1000	–	26.70
FeNaY-2	24.0	230	100–420	850	920	22.80
FeNaY-2	22.0	220	90–410	920	1000	40.60

The dehydration process of Y-type zeolites was reported by Freeman and Caroll [7] as belonging to the reaction type:

$$\mathrm{A(solid)} \rightleftharpoons \mathrm{B(solid)} + \mathrm{C(gas)} \tag{1}$$

which is usually described by the equation:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A_0 \exp\left[-\frac{E}{RT}\right](1-\alpha)^n \tag{2}$$

where n is the order of reaction, α is the degree of conversion, whereas A_0 and E are constants representing the frequency factor and activation energy, respectively. The values of n evaluated from DTA curves by means of Kissinger's [8] method as follows:

$$n = 1.26\sqrt{S} \tag{3}$$

where S is the shape index factor, are close to unity. As the process of dehydration follows first-order kinetics ($n \approx 1$), the values of the 'average' activation

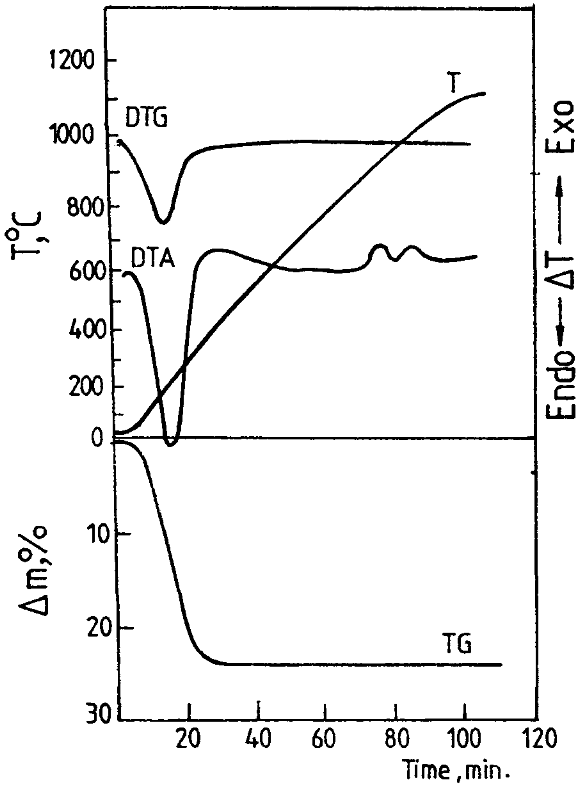

Fig. 1 Typical thermal analysis curves given for 10FeNaY-2 sample

energy may be obtained by applying the Coats-Redfern method [9]. For temperatures lower than T_{peak}, the plot of $\ln\left[-\frac{\ln(1-\alpha)}{T^2}\right]$ *vs.* $\frac{1}{T}$ being a straight line, (Fig. 2), the activation energy can be derived from its slope. The E values, given in Table 2, depend on the nature and amount of cations introduced by ion exchange, proving a stronger bonding of the water molecules in the modified zeolites compared to the parent compounds and suggesting the formation of hydrated clusters [10, 11] in the zeolite cavities.

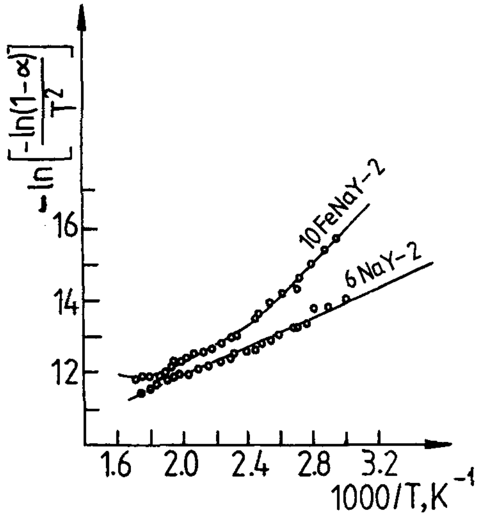

Fig. 2 Linearization of TG curves for 10FeNaY-2 compared to that of 6NaY-2

The first high-temperature exothermic peak at T_1 on the DTA curve is attributed to the structural collapse of the zeolite framework and it is usually taken as a measure of the thermal stability of the zeolite [10]; the second one at T_2, corresponds to the transition to other crystalline phases, as it was confirmed by X-ray diffraction analysis. Although the partial replacement of sodium by hydrogen or multivalent cations results in increased values of T_1 as compared to the parent NaY zeolites, (Table 2), the XRD data do not always confirm an enhanced thermal stability.

X-ray diffraction analysis

The X-ray powder patterns obtained at room temperature by a DRON-3 apparatus, by means of Cu_K radiation (λ = 1.54178 Å) were in agreement with literature data [12, 13], confirming well crystallized starting materials.

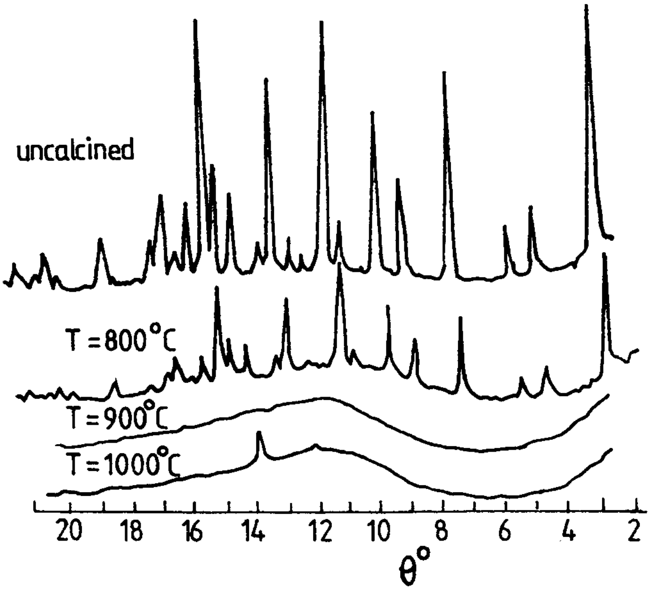

Fig. 3 X-ray patterns of NaY-2 calcined at different temperatures

The thermal stability was monitored by investigation the samples heated for 4 h in air at different temperatures from 300 to 1100°C and then rehydrated in air at room temperature for 24 h. The spectra of samples calcined at high temperatures (Fig. 3) reveal changes in the crystallinity degree, i.e., the gradual break-down of the zeolite framework and a transition into other crystalline phases such as mullite, crystobalite or quartz. As in the investigated materials the lattice collapse begins at temperatures, T_{amf}, lower than the value corresponding to the T_1 peak values of the DTA curves, we suggest the temperature T_{amf} to be taken as a measure of the thermal stability of the zeolite. This temperature, (Table 3) depends on the nature and concentration of the cations introduced by ion exchange. For rare-earth and hydrogen-containing zeolites both the exothermic T_1 and the T_{amf} values reveal the enhancement of the thermal stability. For iron-exchanged zeolites, though the values of T_1 increase as compared to that of the NaY, the framework break-down begins at temperatures lower than that corresponding to the parent zeolite, the values of T_{amf} depending on the amount of iron ions.

By comparing the XRD spectra of the modified zeolites with those of the parent zeolite it was established that the relative intensity of the peaks and d-spacings are dependent on both the degree of the cation exchange and the nature of cations. For example, samples containing rare-earths exhibit diffractograms in which the intensity of the peak corresponding to the 311 plane is diminished and the peaks 220, 620 and 444 are missing. It seems likely that the multivalent cations and hydrogen may not hold the same sites as those held by the alkali metal ions and hence the ion exchange can determine the modifications of the framework stability.

The lattice constant, a_o, was calculated by averaging the values $a_{hkl}=\sqrt{h^2+k^2+l^2}\cdot d_{hkl}$ (cubic lattice) obtained from the Bragg spacings of the reflexion with angles greater than 10°, for which the error of ±0.05° gives rise to an uncertainty in a_o within 0.025 Å.

The cation exchange modifies the unit cell size, the uncalcined ReNaY and HNaY zeolites show lattice contractions, while the ones exchanged with iron show lattice dilations, as compared to the unit cell of the parent samples. By plotting the values of the lattice constant of uncalcined zeolites versus the corresponding T_{amf} temperature, (Fig. 4), one can relate the thermal stability of the modified zeolites to their unit cell dimensions, a smaller value of a_o being connected to a higher stability [14]. Among the investigated samples the proton-containing ones turned out to be the most stable, while the iron-exchanged ones are the most unstable.

Table 3 Lattice constants at different calcination temperatures

Samples	a_o ±0.025(Å)						T_{amf} /
	uncalcined	600°C	700°C	800°C	900°C	1000°C	°C
NaY-1	24.57	24.59	24.61	24.50			820
ReNaY-1	24.50	24.52	24.53	24.55	24.55		910
HNaY-1	24.39	24.34	24.33	24.36	24.38	24.40	1000
FeNaY-1	24.61	24.62	24.62	24.58	24.55		800
FeNaY-1	24.62	24.57	24.56	24.53	24.58		770
NaY-2	24.52	24.51	24.51	24.63			720
ReNaY-2	24.46	24.49	24.50	24.54	24.54		820
HNaY-2	24.40	24.35	24.34	24.39	24.38	24.22	900
FeNaY-2	24.62	24.60	24.52	24.62			650
FeNaY-2	24.61	24.58	24.53	24.52			650

By following the dependence of the unit cell dimensions on the activation temperatures, diagrams like the one given in Fig. 5 can be obtained. The most important feature of the diagram is the minimum in a_o reached upon heating the sample at a certain temperature T_o, which turned out to be that of the treatment which improved the thermal properties of the zeolite. The sample HNaY-2 reaches the minimum in lattice dimension of a_o^{min} = 24.34 Å upon activation at

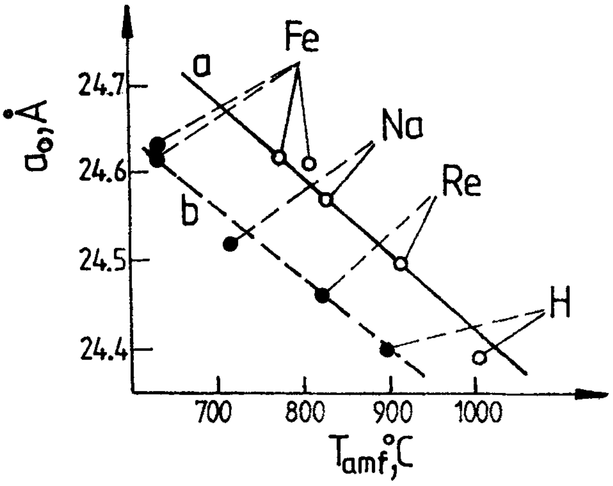

Fig. 4 Correlation of XRD structural collapse temperature, T_{amf}, with the unit cell size for modified zeolites derived from the parent zeolites: (a) NaY-1 and (b) NaY-2, respectively

temperature $T_0 = 700°C$. One can see that the point of maximum with $a_0^{max} = 24.40$ Å corresponds to the temperature $T_{amf} = 900°C$ at which the crystalline-amorphous phase transition begins. The last part of the diagram reflects the heterogeneity, from the point of view of the lattice constant values, of the crystallites constituting the investigated zeolitic material. By heating a sample at temperatures higher than T_{amf}, the amorphous phase coexists with the zeolitic one. The undamaged crystallites are those which have lattice constants lower than a_0^{max}. The structural and thermal heterogeneity explains the large range of temperatures, $\Delta T \approx 100°C$ in which the crystalline-amorphous phase transition takes place.

Discussion and conclusions

The combined thermal analysis and X-ray diffraction method provides useful information on the thermal properties of Y-type zeolites modified by ion exchange with rare-earths, proton and iron ions, respectively.

Of the two parent zeolites, with different content of iron and manganese as trace impurities, the NaY-1 type turned out to have the greatest thermal stability.

As the activation energies of the dehydration process for the two parent zeolites are very close, i.e., $E_a = 18.66$ kJ/mol for NaY-1 and $E_a = 18.70$ kJ/mol for NaY-2, it may be inferred that the same number of ions move almost freely in

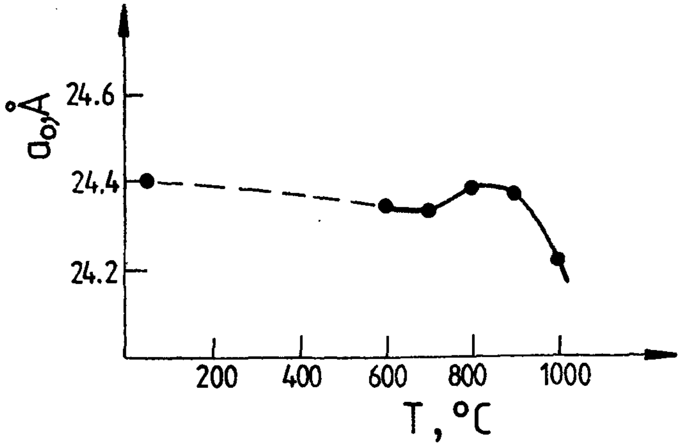

Fig. 5 Lattice constant *vs.* the temperature of activation for sample HNaY-2

the zeolite water, whereas the impurities contained in excess in the NaY-2 isomorphously replace the aluminium ions in the zeolite framework [3] resulting in a decreased thermal stability. The increased values of the activation energy of zeolites modified by ion exchange compared to those of the parent samples prove that the water molecules are more strongly bonded to the multivalent cations and protons.

The hydroxide type clusters may be formed in zeolite cavities as it was also evidenced [3, 15, 16] by electron paramagnetic resonance method.

The cation exchange induces changes in the lattice stability, i.e., an increase of about 180°C for the HNaY sample, and of about 100°C for the ReNaY one, and a decrease of about 50°C for the FeNaY samples.

The first exothermic peak at T_l in the DTA curve should be used with great caution as a measure of the lattice stability. We suggest the temperature T_{amf} derived by XRD-analysis as an unambiguous measure of the thermal stability of zeolites. This is the temperature at which the lattice collapse begins and which may be related to the structural characteristics of zeolites such as unit cell dimensions. A decrease in the lattice constant may be connected with an increased T_{amf}, while an increased lattice constant results in decreased value of T_{amf}. By activating a sample at a certain characteristic temperature T_o, one can enhance its thermal stability, resulting a minimum in the lattice constant. The XRD studies also evidenced the heterogeneity of the lattice constants of the zeolite crystallites which may result in different values of T_l and T_{amf}.

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Zusammenfassung — Mittels TG-DTA-DTG und Röntgendiffraktionsspektroskopie wurden die thermischen und strukturellen Eigenschaften von zwei NaY-Zeolithen und von deren durch Ionenaustausch modifizierten Derivaten (ReNaY, HNaY, FeNaY) untersucht. Sowohl dem Wasser innerhalb des Kristalles als auch dem Zeolith-Netzwerk gebührte unsere Aufmerksamkeit. Die im Gitter lokalisierten Verunreinigungen (Fe) als auch die durch Ionenaustausch eingebrachten Ionen (Re, H, Fe) beeinflussen die Eigenschaften der Zeolithe. Die Werte der Aktivierungsenergie des Dehydratationsprozesses beweisen, daß die Wassermoleküle in allen modifizierten Proben stärker gebunden sind, als in den Stammverbindungen. Bezogen auf NaY-Zeolithe wurde für ReNaY eine gesteigerte thermische Stabilität von etwa 100°C und für HNaY von etwa 180°C gefunden, für FeNaY-Proben eine reduzierte Stabilität von etwa 50°C. Die Temperatur T_{amf}, bei welcher der Gitterzusammenfall einsetzt und die anhand von Röntgendiffraktionsbildern für in Luft zwischen 300 und 1100°C erhitzte Proben geschätzt wurde, ist jene Temperatur, die mit den strukturellen Eigenschaften von Zeolithen in Zusammenhang gebracht werden kann, d.h. zur Gitterkonstante der unkalzinierten Substanzen. Die Röntgendiffraktionsuntersuchungen zeigen sowohl hinsichtlich der Gitterkonstantenwerte als auch der thermischen Stabilität die Heterogenität der Kristallite, die das Zeolithmaterial bilden.

Da die Temperatur T_{amf} im allgemeinen nicht mit der Temperatur des ersten exothermen Peaks zusammenfällt, schlugen wir vor, die Temperatur T_{amf} als ein eindeutiges Maß für die thermische Stabilität anzusehen.