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THERMAL AND STRUCTURAL PROPERTIES OF RARE EARTH EXCHANGED ZEOLITES*

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A series of rare earth zeolites of types X and Y were prepared by cation exchange. Thermal analysis curves (TG/DTA) were employed to estimate the structural changes in the zeolite framework. Analogous investigations were carried out by independent methods such as XRD and IR spectroscopy. The results indicate increased thermal stability on the replacement of sodium by rare earth. Partial replacement of rare earth by ammonium/hydrogen enhances the thermal stability. The type Y zeolites are more stable than those of X type.

During the past decade the use of molecular sieve zeolites has increased tremendously due to their wide range of applications in the petrochemical industry. The rare earth exchanged zeolites of types X and Y have been extensively used as catalysts [1–3] for petroleum cracking and hydrocarbon conversion reactions. Their physicochemical properties are of direct significance in relation to the catalytic activity. High thermal stability is one of the important prerequisites for solid catalysts such as zeolites. The thermal stability of the zeolite framework depends [4] considerably on the type of cation, their distribution among the non-framework sites, and the degree of cation exchange. Cation exchange with multivalent cations and/or hydrogen enhances [4] the thermal stability. It was therefore thought interesting to investigate the structural and thermal properties of series of rare earth exchanged X and Y type zeolites by XRD, IR spectroscopy, TG and DTA.

Experimental

The crystalline zeolite of type X was prepared in the laboratory [5]. The type Y zeolite (SK-40) was obtained from Union Carbide Corporation (USA). The cation exchange was carried out by contacting the zeolite powder with 5% mixed rare earth chloride ($RECl_3$) solution at 95° in the conventional way [6]. $RECl_3$ was prepared by dissolving pure rare earth oxide (obtained from Indian Rare Earth Ltd. and composed of lighter rare earths such as La, Pr and Sm with traces of heavy rare earths) in analar grade hydrochloric acid. Repeated cation exchange treatments were employed to obtain samples with a higher degree of cation exchange. Ammo-

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Table 1

Anhydrous compositions of the zeolites

NaX: $Na_{85}(AlO_2)_{85}(SiO_2)_{107}$
NaY: $Na_{55}(AlO_2)_{55}(SiO_2)_{121}$

Zeolite	Cations/unit cell			% Exchange
	Na^+	Re^{3+}	H^+	
NaX	85	–	–	–
RE(1)X	9.5	21.0	12.5	88.0
RE(2)X	8.0	22.0	11.0	91.0
RE(3)X	4.5	23.0	11.5	94.4
RE(4)X	2.5	23.8	11.1	97.1
REHX	2.4	22.5	15.1	97.3
NaY	55	–	–	–
REY	2.5	17.5	–	95.9
REH(1)Y	2.2	15.9	5.1	95.8
REH(2)Y	1.6	12.1	17.1	97.2

nium exchange was carried out by contacting the RE^{3+} exchanged sample with 5% NH_4Cl at 95°. By calcining the sample at 400° it was subsequently reduced to the hydrogen form. However, REH(2)Y was prepared from the zeolite NaY by first exchanging with NH_4^+ and then with RE^{3+} cations. The compositions of the exchanged samples were determined by gravimetric analysis. The unit cell compositions calculated from the analytical data are given in Table 1. The cation deficiency arises [7, 8] from hydrolytic replacement of cations (mostly Na^+) by H_3O^+ during the process of washing and cation exchange and is compensated by H^+ in the unit cell in Table 1. The total number of H^+ ions in the unit cell involves those introduced via ammonium exchange and those incorporated by hydrolytic exchange during washing.

The thermal analysis curves (DTA and TG) were simultaneously recorded on an automatic [MOM, Budapest, Hungary, type OD-102] derivatograph described by Paulik et al. [9]. About 200 mg sample was placed in the platinum crucible for the measurements and precalcined alumina was employed as a reference standard. All samples were heated in an air atmosphere at a constant heating rate of 10 deg/min up to a maximum temperature of 1200°, sensed through a Pt/Rh thermocouple. The IR spectra of zeolite samples in nujol mull were recorded on a Perkin-Elmer 221 spectrometer in the frequency range 250–700 cm^{-1}. The X-ray powder patterns of hydrated zeolite samples were recorded on a Philips X-ray unit with a Debye-Scherrer Camera, using nickel filtered CuKα radiation (λ = 1.540 Å).

Results and discussion

X-ray powder patterns

The relative intensities and *d* values for the parent zeolites X and Y and for two exchanged samples with maximum degree of cation exchange are presented in Table 2. The X-ray data for the parent zeolites NaX and NaY are in agreement with the data reported earlier [10]. The X-ray powder patterns revealed that, in general, the crystalline character of the zeolites is retained even after severe (97%) cation exchange. However, the intensities of the peaks corresponding to the 220 and 311 planes diminish with increasing rare earth content. The lines are absent in the case of the zeolite RE(4)X due to weakening of the lattice [11] at the higher degree of cation exchange, and the higher scattering factor of heavy rare earth ions. A similar XRD pattern has been reported [12] in the case of REY. It also seems likely that the multivalent ions may not occupy positions coincident with those occupied by the alkali metal cations.

Table 2

X-ray data on rare earth exchanged X and Y type zeolites

NaX			RE(4)X			NaY		REY	
hkl	*d*, Å	*I*	*d*,Å	*I*	*hkl*	*d*, Å	*I*	*d*, Å	*I*
111	14.34	VS	14.62	VS	111	14.43	VS	14.34	VS
220	8.77	MS	—	—	220	8.73	W	—	—
311	7.43	M	—	—	311	7.46	W	6.91	W
331	5.73	MS	6.16	W	311	5.68	W	5.74	W
333	4.76	W	4.77	W	333	4.76	W	4.85	W
440	4.39	M	4.38	W	440	4.38	MS	4.32	W
620	4.09	VW	4.13	W	533	3.71	S	3.71	S
622	3.77	S	3.77	S	711	3.43	VW	3.42	W
711	3.53	W	3.49	W	642	3.28	S	3.26	M
642	3.31	S	3.31	S	822	2.87	W	2.89	M
822	2.92	W	2.93	M	751	2.84	MS	2.84	M
751	2.85	S	2.88	M	911	2.72	VW	2.70	VW
840	2.78	M	2.79	S	931	2.61	MS	2.61	MS

VS — Very strong
S — Strong
MS — Medium strong
M — Medium
W — Weak
VW — Very weak

Infrared analysis

The IR spectra of X and Y type zeolites are shown in Fig. 1. The bands at 667, 560 and 460 cm^{-1} are assigned [13] to symmetric stretch ($O \leftarrow T \rightarrow O$), double ring (6DR) and T–O bending, respectively, while the bands at 408, 367 and 344 cm^{-1} are assigned to pore opening in the zeolites. The absorption bands are sharper for NaX than for NaY due to the lower silica/alumina ratio. The intensity of the bands depends [13, 14] not only on the crystallinity but also on the Si/Al ratio; the bands at 575 cm^{-1} and 460 cm^{-1} are sharper for a lower Si/Al ratio. The present data confirm the data reported by Flanigan and coworkers [13]. The sharper bands at 575 cm^{-1} and 465 cm^{-1} for NaX become broad and less intense on Re^{3+} exchange, while those at 667, 408 and 367 cm^{-1} become very weak for zeolites RE(3)X and Re(4)X. This could be attributed to the partial weakening of the lattice [14, 15].

In the spectra of Y type zeolites, the bands at 578, 453, 380 and 328 cm^{-1} are in accordance with the literature [13, 15]. In contrast to the X type zeolites, the broad and less intense bands for NaY at 578 cm^{-1} and 453 cm^{-1} become more intense and sharper on the introduction of $\mathrm{RE}^{3+}/\mathrm{H}^{+}$ ions. Calculation of the lattice energy of various zeolites [16] revealed that the zeolite lattice is stabilized by increase of the silica/alumina ratio. Moreover, the replacement of univalent sodium by di- or trivalent cations also leads to an increase in crystal lattice energy [16] and hence structural stability. The IR results support the above data and indicate that, upon

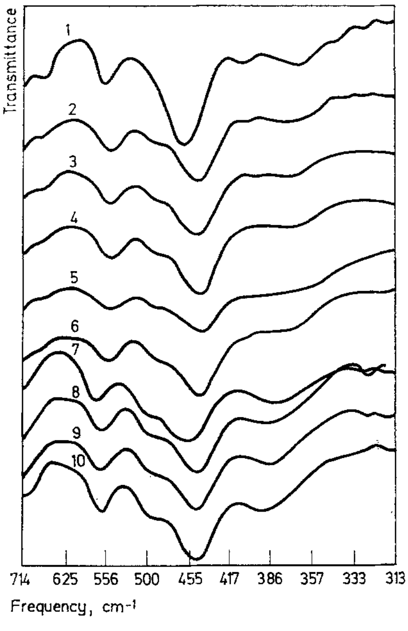

Fig. 1. Infrared spectra of X type zeolites

cation exchange with Re^{3+}/H^+, the enhancement in the structural stability is greater in Y type zeolites with a higher silica/alumina ratio than in X type zeolites with a lower silica/alumina ratio.

Thermal analysis

Typical thermal analysis curves for RE(4)X are presented in Fig. 2; the DTA curves for the X and Y types are shown in Fig. 3. The zeolites undergo endothermic changes between 50 and 450°, due to the desorption of zeolitic water. With increasing rare earth content, the peak temperature of the DTA endotherm increases from 130 to 180° and from 150 to 210° for X and Y type zeolites, respectively. This suggests that water molecules are more strongly bonded to RE^{3+} cations than to Na^+ cations. The relevant data are summarized in Table 3. A weak and very broad endotherm at ~600° is due to dehydroxylation. The high-temperature exotherm is attributed to a structural collapse or phase transformation [10] and it is taken as a measure of the thermal stability [4] of the zeolite. Zeolites NaX and NaY are generally stable up to 800°, as is evident from Fig. 3. On increase of the RE^{3+} content in X type zeolites, the thermal stability increases from 810 to 930° (Table 3).

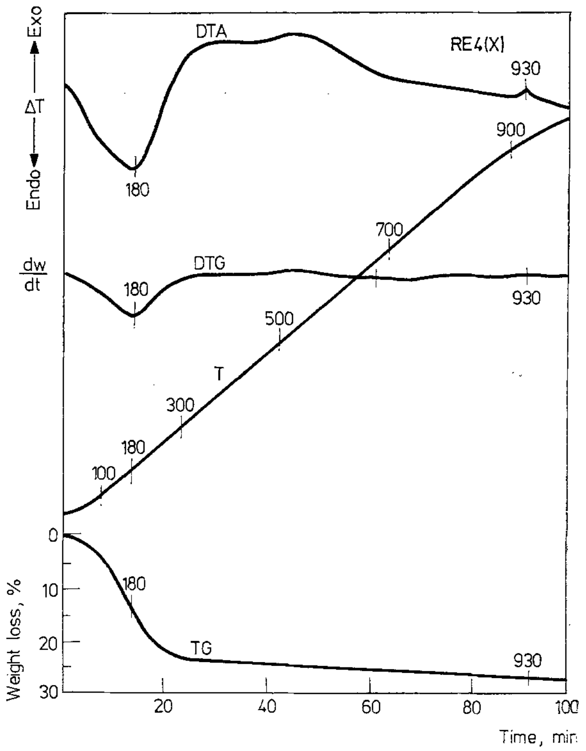

Fig. 2. Typical thermal analysis curves for RE(4)X

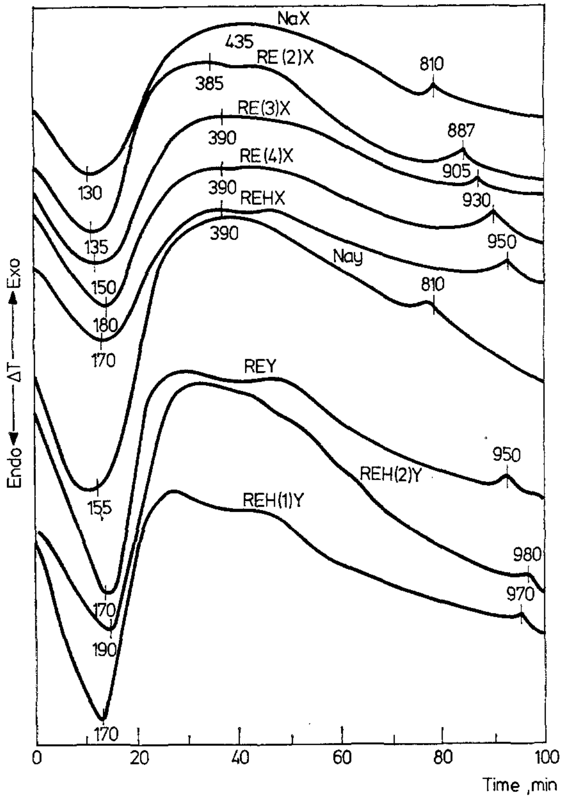

Fig. 3. DTA curves for rare earth exchanged X and Y type zeolites

Table 3

Thermal analysis data on rare earth exchanged zeolites

Zeolites	% Loss in wt. from TG	Temperature, °C of Min. of endothermic peak	Temperature, °C of Complete dehydration	Temperature, °C of Max. of exothermic peak	Activation energy for (*E*) dehydration kJ/mole
NaX	25.50	130	435	810	19.5
RE(1)X	23.50	127	410	845	28.4
RE(2)X	23.25	135	385	887	19.6
RE(3)X	23.00	150	390	905	22.9
RE(4)X	22.50	180	390	930	22.6
REHX	22.25	170	390	950	21.5
NaY	23.50	155	395	810	23.8
REY	21.75	170	360	930	23.3
REH(1)Y	21.50	190	490	970	21.4
REH(2)Y	22.50	170	480	980	25.0

Moreover, the thermal stability of the rare earth zeolite is further enhanced on partial replacement of RE^{3+} by NH_4^+ (subsequently reduced to H^+), as is indicated by the higher structural breakdown temperature (950°) of REHX. The results are in agreement with reported data [17].

The enhancement in thermal stability upon rare earth exchange is higher in the case of Y type zeolites, as evidenced from the exothermic peak temperatures of REY (950°), REH(1)Y (970°) and REH(2)Y (980°). The partial replacement of RE^{3+} by NH_4^+ is also responsible for the increased thermal stability of these zeolites. The zeolite REH(2)Y is somewhat more stable than REH(1)Y, in which the order of introduction RE^{3+} and NH_4^+ is reversed.

TG curves indicated a major loss in weight ($\sim$ 20 – 22%) up to 400 – 450° for all the zeolites studied. With increase of the rare earth content, the TG curves display a comparatively slower dehydration and a decrease in the loss in weight. The loss in weight in the higher temperature range ($>$ 500°) may be due to dehydroxylation. In general, the dehydroxylation of zeolites is slow and occurs in the temperature range 500 – 800° [18]. It may not be accompanied by a distinct weight loss step in the TG curve, but it shows a slow and continuous weight loss up to 1 – 1.5% in this range, as is seen in the case of RE(4)Y in Fig. 2. For NH_4Y, however, a sharp weight loss around 600° has been reported by Ward [19]; this may be due to a larger number of framework hydroxyls associated with the zeolite.

Energy of activation for dehydration

The process of dehydration of zeolites is reported [20, 21] as belonging to the reaction type

$$\text{A (solid)} \rightleftharpoons \text{B (solid)} + \text{C (gas)}$$

and is usually described by the well-known kinetic equation [20]

$$\frac{d\alpha}{dt} = A_0 \exp(-E/RT)\,(1-\alpha)^n \qquad (1)$$

where α is the degree of conversion, and A_0, E and n are constants representing the frequency factor, activation energy and order of reaction, respectively. The values of n evaluated from DTA by Kissinger's shape index method [20] ($n = 1.26(s)^{1/2}$), are found to be nearly equal to 1 (0.95 ± 0.15), which indicates that the dehydration of the zeolites studied follows first-order kinetics. With $n = 1$, Eq. (1) coincides with Barrer's equation [22]; various relationships [21, 23] have been derived from it. The average activation energy values given in Table 3 are evaluated by applying the Coats-Redfern equation [23] to the TG curves and the Piloyan-Novikova equation [21] to the TG and DTA curves. These values of E, however, do not support the earlier conclusion, drawn from DTA endotherms, of stronger bonding of water molecules to the RE^{3+} cations than to the Na^+ ions. Nevertheless, these data do confirm the applicability of different forms of the kinetic equation with $n = 1$. Kissinger's shape index method, in particular, confirms that the process of dehydration of the zeolites studied follows first-order kinetics.

Conclusions

The analysis of thermal analysis curves, such as DTA/TG, provides a useful tool to estimate changes in the thermal properties and modifications in the zeolite lattice as a consequence of cation exchange. Supporting evidence is provided by X-ray powder diffraction patterns and IR spectra. Calculation of the energy of activation for dehydration from DTA/TG curves involves assumptions which are true only under the conditions of constancy of weight and rate of heating of the sample. The results indicate that cation exchange with rare earths increases the thermal stability of the X and Y zeolites; the Y type zeolites exhibit higher thermal stability than the X type zeolites. The order of introduction of the cation also affects the thermal stability of the zeolite.

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ZUSAMMENFASSUNG — Eine Reihe von Ionen der Seltenen Erdmetalle enthaltenden Zeolithen des Typs X und Y wurden durch Ionenaustausch hergestellt. Thermoanalytische Kurven (TG/DTA) wurden zur Beurteilung der strukturellen Veränderungen des Zeolithgitters herangezogen. Analoge Untersuchungen wurden mit unabhängigen Methoden (XRD und IR-Spektroskopie) ausgeführt. Es wurde festgestellt, daß ein Ersatz der Natriumionen durch Ionen der Seltenen Erdmetalle zu einer Erhöhung der thermischen Stabilität führt. Ein teilweiser Ersatz der Seltenen Erdmetallionen durch Ammonium-/Wasserstoffionen erhöht die thermische Stabilität. Zeolithe des Typs Y sind stabiler als die des X-Typs.

Резюме — С помощью катионного обмена был получен ряд цеолитов типа X и У с редкоземельными элементами. Термоаналитические кривые (ТГ/ДТА) были использованы для установления структурных изменений в решетке цеолитов. Аналогичные исследования были проведены такими независимыми методами как рентгено-диффракцией и ИК спектроскопией. Результаты показали увеличение термоустойчивости при замещении натрия на редкоземельный элемент. Частичное замещение редкоземельного элемента на аммоний или водород усиливает термоустойчивость. Цеолиты типа У более устойчивы по сравнению с X типом.