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STUDIES ON THE TEMPERATURE PROGRAMMED DESORPTION OF WATER FROM CoNaX ZEOLITES

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The splitting of water in the temperature range from 470 to 970 K was studied for a series of CoNaX zeolites of a Si/Al ratio of 1.18 and of different degree of exchange and at the parent type NaX. In case of CoNaX zeolites peaks at about 570 and 670 K and a broad flat peak at even higher temperatures could be observed. Both the first peaks are ascribed to the process of dehydroxylation between CoOH and structural OH groups, the latter to the dehydroxylation between structural OH groups only. The parent type provided only a single peak with a maximum at about 570 K.

From the dehydroxylation peaks activation parameters have been calculated and a scheme has been suggested for the mechanism.

Introduction

The water content of zeolites as well as its change occurring during the course of thermal treatment strongly influence the state of the exchanged cations and of the framework and therefore also acidity and catalytic properties.

X-ray diffractometric [1], ir and uv spectroscopic [2-7], magnetic [8, 9] and thermodesorptometric [7, 10] studies, carried out on CoX and Y zeolites show the cobalt ions in the fully hydrated state to be existing as $[Co(H_2O)_6]^{2+}$ complexes. When thermal dehydration starts these complexes are maintained in the supercages while inside the sodalite units Co^{2+} is found fourfold coordinated by water. During further dehydration (increasing temperature) cobalt ions are transferred from $[Co(H_2O)_4]^{2+}$ via $[Co(Ox)_3(H_2O)_3]^{2+}$ to $[Co(Ox)_3H_2O]^{2+}$ in the supercage as well as in the sodalite cage, and, finally, at very high temperature after having lost the last water, to $[Co(Ox)_6]^{2+}$ in the hexagonal prisms.

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Simultaneously with these processes OH groups are formed according to

$$Co^{2+} + H_2O + ZO^- \rightarrow CoOH^+ + ZOH$$

(ZO^- anionic lattice, ZOH structural OH group), as described repeatedly [11, 12], which disappear again at higher temperatures according to the reverse process (dehydroxylation). Above 600...700K processes like

$$CoOH^+ + Co^{2+} + ZO^- \rightarrow [(Ox)_3\text{-}Co\text{-}O\text{-}Co\text{-}(Ox)_3]^{2+} + ZOH$$

take place.

Tpd investigations were carried out in order to obtain kinetic and mechanistic data of dehydratation and dehydroxylation processes and to establish temperature ranges of these processes.

Experimental

For the studies the following series of CoNaX zeolites of different degree of exchange was available, prepared by ion exchange from the parent NaX type: 0.15 CoNaX; 0.32 CoNaX; 0.54 CoNaX and 0.77 CoNaX.

The desorption apparatus consisted of an oven of low inertia, equipped with two thermocouples of low inertia for controlling and measuring the temperature, of a quartz reactor of about 1 cm diameter, of an electronic temperature controller and a thermo-conductivity cell.

0.1 g of zeolite were used pelleted to grains of 0.2...0.4 mm size, diluted by 1 g of quartz of equal size and equilibrated in a desiccator over saturated $Ca(NO_3)_2$ solution.

Temperature programmed desorption (tpd) was carried out in an extremely dry He stream (3 l per hour) using heating rates from 1 to 20 K per min but mainly 10 K per min. As strongly overlapping peaks were observed (see Fig.1) the following method of peak separation was used: First of all physisorbed water was removed by heating up to 470 K and the temperature was kept at this level till the base line of the recorder was reached again. Then the heating programme was continued up to the next peak maximum, the temperature kept constant again till reaching the base line and so on. Calibration enabled calculation of the water amounts from the areas of the tpd peaks obtained.

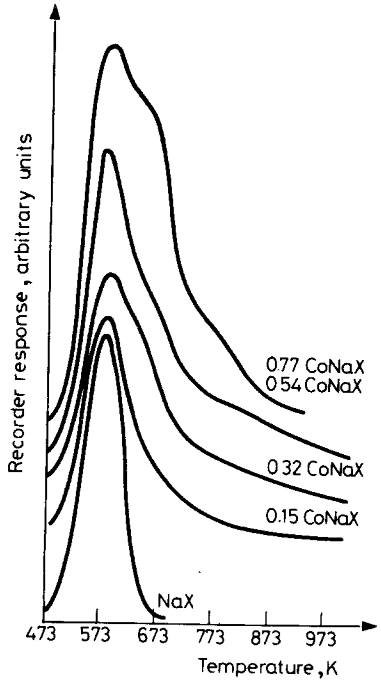

Fig. 1 Desorptogrammes of water of NaX and of a series of CoNaX samples

Results and discussion

Results of water tpd from CoNa and NaX samples are shown in Fig. 1. One can see that in the case of CoNaX zeolites several overlapping peaks exist while for the parent NaX type only a single peak is observable. In the case of the CoNaX row the water amount desorbed above 470K is about proportional to the exchange degree. In Fig. 2 results of peak separation by means of the stop method (see Experimental) are shown.

The peak with a maximum at about 570 K, which in the literature is often ascribed to chemisorbed water, should really represent a dehydroxylation process because the catalytic activity in but-1-ene isomerization on CoNaX and Y zeolites [13, 14] dramatically decreases after removal of the water belonging to this peak. Other authors [15] also found maximum catalytic activity in connection with activation temperatures lower than 600 K (using in this case REY zeolites). The peak at 670 K and a broad flat peak at a higher temperature also result from dehydroxylation processes but of different kind.

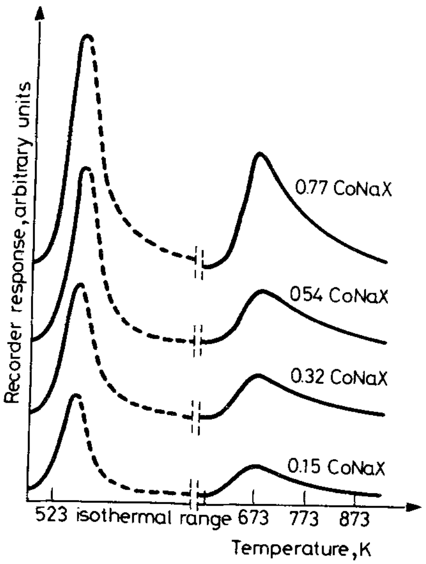

Fig. 2 Tpd spectra of water of a series of CoNaX zeolite; separation of the 570 K peak from the remaining spectrum by stopping of the temperature programme at the maximum of the 570 K peak

When considering ir spectra of cobalt zeolites [7] representing the same level of activation as in case of tpd experiments on may see the largest part of OH groups to be bound in associated structures. When additionally taking into account that on this level of activation only about one water molecule per Co^{2+} is situated inside the zeolite (see Table 1) it is most probable that the water peak with a maximum at 570 K results from a dehydroxylation process between $CoOH^{+}$ and structural OH groups which are situated in the supercage and connected via a hydrogen bridge, so explaining also the facility of dehydroxylation and the low temperature of this process, respectively. The 670 K peak then should represent dehydroxylation between isolated $CoOH^{+}$ and structural OH groups, and the water splitting at higher temperatures dehydroxylation steps between structural OH groups (see also [16]). Scheme 1 summarizes the conditions.

Further interesting and more exact statements should be expected from kinetic calculations on the basis of tpd spectra: As described frequently tpd results can be obtained by the heating-rate variation method on the one hand and on the basis of the linearized differential rate equation on the other. In order to obtain realistic information about the kinetics beside these methods an isothermal evaluation was used and the Arrhenius parameters were calculated (see Fig. 3).

Table 1 Water amounts desorbed from a series of CoNaX zeolites

Zeolites	Mg water per gr zeolite		Molecules water per Co^{2+}		Sum
	570 K peak	Peaks at high temp.	570 K peak	Peaks at high temp.	
0.15CoNaX	6.5	3.9	0.71	0.43	1.14
0.32CoNaX	9.8	5.7	0.53	0.31	0.84
0.54CoNaX	11.8	8.4	0.38	0.27	0.65
0.77CoNaX	18.0	15.0	0.42	0.35	0.77
NaX	13.3	-	0.45[1]	-	0.45[1]

[1] molecules water per Na+

Additionally, rate constants from the isothermal part of the desorption curve (Fig. 2, dashed lines behind the peak maxima) were calculated and compared with such ones calculated from the Arrhenius parameters obtained from the non-isothermal part of the desorption peak (part before reaching the peak maximum). The latter method provided the following results:

1/ the isothermal part can be well evaluated by a 1st order rate law.

room temp. $Me^{2+}(H_2O)_n \rightarrow Me^{2+}(H_2O) + (n\text{-}1)\ H_2O$
to $Me^{2+}(H_2O) \rightarrow MeOH^{+} + H^{+}$
470 K $ZO^{-} + H{+} \rightarrow ZOH$
470...670 K: $MeOH^{+} + ZOH)_{assoc.} \rightarrow Me^{2+} + ZO^{-} + H_2O$
620...720 K: $MeOH^{+} + ZOH \rightarrow Me^{2+} + ZO^{-} + H_2O$
above 670 K: $MeOH^{+} + Me^{2+} \rightarrow [Me\text{-}O\text{-}Me]^{2+} + H^{+}$
$ZO^{-} + H^{+} \rightarrow ZOH$
above 770 K: $2\ ZOH \rightarrow Z\text{-}O\text{-}Z + H_2O$

Scheme 1

2/ Isothermal and non-isothermal results agree only when 1st order kinetics are assumed. Thus it can be stated that a first-order irreversible desorption model fits the kinetic results best.

In Table 2 the Arrhenius parameters can be seen. The results shown in Table 2 indicate a good agreement between the methods used. When comparing the results of the high and the low-temperature peaks a difference in activation energy of about 40...50 kJ per mole is obtained. When, as assumed above, the low temperature peak is ascribed to dehydroxylation of associated OH groups and the high-temperature one to the same process of isolated OH groups then the difference of activation energies could represent a measure for the hydrogen bridge energy. The value above is in good agreement with data for hydrogen bridges of medium strength [17].

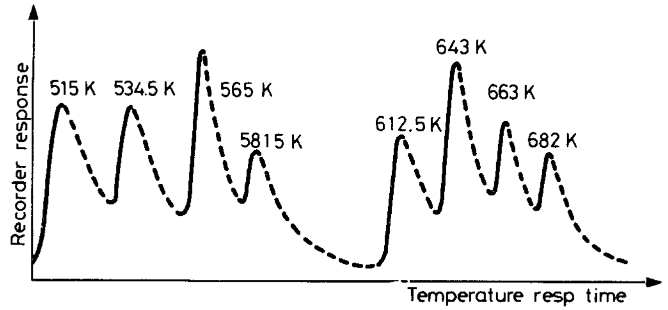

Fig. 3 Tpd spectrum of water from a 0.54 CoNaX sample; splitting of the peaks into anisothermal and isothermal ranges by repeated stopping of the temperature programme (solid lines: anisothermal ranges; dashed lines: isothermal ranges)

Only a few results with respect to water splitting from zeolites are described in literature.

The reaction order of 1 was also found by other authors for water desorption. Kulkarni *et al.* [18] studied water desorption from $Fe^{3+}Y$ zeolites by DTA methods. They found peaks in the 570 and 670 K region, using heating rates of 10 deg/min. The peaks could be evaluated in terms of first order kinetics.

Dondur [19] reported about water desorption from A zeolites exchanged with alkali and some bivalent cations. In the latter case activation energies of 75...80 kJ mole^{-1} were found for water desorption in a comparable range of temperature.

Stach [20] found in case of CaNaA zeolites adsorption heats between 45 and 145 kJ mole^{-1} depending on the degree of coverage with water.

When considering our explanation for water splitting from CoNaX zeolites in the 573 K region to be brougth about by recombination of $MeOH^+$ and structural OH groups, bound by hydrogen bridges an answer must be found on the question why water splitting from parent type NaX samples occurs at the same temperature and with similar activation energy although the latter process cannot be explained by dehydroxylation but only by dehydration. Important statements about the structure of water in parent-type faujasites were made by Pfeifer *et al.* [21, 22] using measurements of proton-magnetic relaxation times for NaY samples. Especially samples with small amounts of water which correspond to the degree of dehydration of our samples activated up to 470 K showed an addition of water molecules with their oxygen to non-localized sodium cations. One of the water protons was found to be free while the other formed a hydrogen bridge to framework oxygen. The distance from proton to proton was remarkably greater than in the case of free water molecules.

Table 2 Activation parameters of dehydroxylation of CoNaX and NaX zeolites determined by different methods (E_a in kJ per mole, A in min^{-1})

Zeolites	Heating rate var. meth.	Linearized diff. equation method		Isothermal / anisothermal method	
	Peak: 570 K	Peak: 570 K	670 K	Peak: 570 K	670 K
NaX	E_a : 67.6	E_a :73.6			
	A : 2.36x10^4	A :6.25x10^5			
0.15 CoNaX		E_a : 92.7			
		A :6.01x10^7			
0.32 CoNaX		E_a : 82.3			
		A : 5.27x10^6			
0.54 CoNaX	E_a :79.8	E_a : 85.7	125.6	E_a : 74.1	113,2
	A : 2.01x10^6	A : 1.33x10^7	1.43x10^8	A : 4.06x10^5	7.57x10^7
0.77 CoNaX	E_a :78.3	E_a : 83.7	141.9	E_a : 70.9	120.4
	A :5.79x10^6	A : 5.91x10^6	1.95x10^9	A : 1.70x10^5	1.72x10^8

Thus the process of water splitting in the 573 K region in both cases (CoNaX and NaX) could occur according to similar mechanisms and also the same kinetics with similar activation energies.

Because of the inability of univalent cations like Na^+ for complete water splitting in faujasites no processes according to steps (3)...(5) of scheme 1 can occur and therefore no tpd peaks are observed at higher temperatures.

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Zusammenfassung — Im Temperaturbereich von 470-970 K wurde bei einer Reihe CoNaX Zeolithen mit einem Si/Al-Verhältnis von 1.18 und einem unterschiedlichen Austauschgrad sowie bei dem NaX Stammtyp die Abspaltung von Wasser untersucht. Im Falle von CoNaX Zeolithen können Peaks bei 570 und 670 K und ein breiter flacher Peak bei noch höheren Temperaturen beobachtet werden. Die beiden ersten Peaks werden dem Prozeß der Dehydroxylierung zwischen CoOH- und strukturellen OH-Gruppen, letzterer der Dehydroxylierung nur zwischen strukturellen OH-Gruppen zugeschrieben. Der Stammtyp ergibt nur einen einzigen Peak mit einem Maximum bei 570 K. Aus den Dehydroxylierungspeaks wurden Aktivierungsparameter berechnet und ein Mechanismusschema entwickelt.