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THERMOANALYTICAL INVESTIGATIONS ON ION-EXCHANGED Y-ZEOLITES

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NH_4Y and NH_4LaY-type zeolite catalysts were prepared by cyclic ion-exchange of a synthetic Linde Y-zeolite. The release of ammonia and water were followed by evolved gas analysis (automatic thermogastitrimetric equipment) as well as with a continuous selective water detector.

The ion-exchangeability of NH_4^+ for La^{3+} on the zeolite was also investigated. The capacity of the NH_4Y-zeolite was found to be 3.60 mequiv./g calcined zeolite. After a three times repeated ion-exchange process, 88.9% of the ammonia was replaced by lanthanum.

Synthetic Y-zeolites are widely used as catalysts in the alkylation of isoparaffins with olefins, due to their higher activity and thermal stability. HY-zeolites are prepared by calcination of the NH_4Y form, accompanied by liberation of ammonia and water [1, 2]. The proton formed reacts with lattice oxygen to form hydroxyl groups.

Ward investigated the variation of the water and ammonium ion contents of the zeolite as a function of temperature by infrared spectroscopy as the temperature was raised stepwise from ambient up to 600° [1]. The intensity of the 1640 cm^{-1} band was used as an indicator of the amount of water on the zeolite, while the band at 1485 cm^{-1} was used to indicate the variation of the ammonium ion. It was found that most of the water was removed by 250° and most of the ammonium ion decomposed between 200° and 350°.

According to the literature [3], lanthanum has a marked stabilizing effect on Y-type zeolite catalysts, and the presence of La^{3+} in the zeolite structure increases their activity and thermal stability in alkylating reactions.

In the present study thermoanalytical investigations were carried out on NH_4Y and NH_4LaY-form zeolites for the continuous and selective monitoring of ammonia and water release and to follow the $NH_4^+ \rightarrow La^{3+}$ ion-exchange process.

Experimental

Materials used

Union Carbide LZ-452 type synthetic Y-zeolite with a SiO_2/Al_2O_3 molar ratio of 4.91 was applied. The composition of the zeolite in water-free form was the fol-

lowing:

Al_2O_3	22.2%
SiO_2	64.5%
Na_2O	12.7%

In the air-dried form the water content was about 24% and the specific surface area was 902 m^2/g.

NH_4Y-form zeolite was prepared by three times repeated ion-exchange of the Linde Y-zeolite with 2.5 *M* NH_4NO_3 solution.

The NH_4LaY forms were made from the NH_4Y one by stepwise ion-exchange of NH_4^+ for La^{3+} by treatment with 2.5 *M* $La(NO_3)_3$ solution. In this way mixed ammonium-lanthanum forms designated $NH_4LaY_{(1)}$, $NH_4LaY_{(2)}$ and $NH_4LaY_{(3)}$ were produced, according to the number of cycles repeated.

Instrument

Evolved gas analyses were carried out with thermogastitrimetric equipment (TGT) attached to a derivatograph (MOM, Budapest). The samples were heated at a rate of 5°/min. The evolved gases were collected and absorbed in water by dry nitrogen carrier gas at a flow rate of 6 dm^3/h.

A continuous selective water detector [4] was also used (directly combined with the derivatograph) to investigate the water-releasing process.

Procedure used

150–500 mg air-dried samples were heated up to 600° and the T, TG, DTG, DTA, TGT and DTGT curves were simultaneously recorded.

The liberation of ammonia from the sample was followed by automatic acid-base titration, using 0.1 *M* HCl as a titrant and potentiometric end-point indication.

A water detector was also used under the same experimental conditions.

Results and discussion

Figure 1 shows the thermoanalytical curves of the NH_4Y-zeolite sample, including the water detector trace. Water was released in different stages and the first step was completed by 300°. Above this temperature structural water was evolved up to 650°. At 640° a separate step can be observed.

Ammonia started to evolve at 200° and two overlapping steps can be seen at 300° and 370°. The liberation of ammonia was completed by 550°. The amount of ammonia was calculated from four parallel measurements. The data obtained and the relative errors are given in Table 1.

The titration curves of the NH_4Y, $NH_4LaY_{(1)}$, $NH_4LaY_{(2)}$ and $NH_4LaY_{(3)}$ samples are shown in Fig. 2. By comparison of the corresponding curves, the $NH_4^+ \rightarrow La^{3+}$ ion-exchange process can be followed as a function of the number

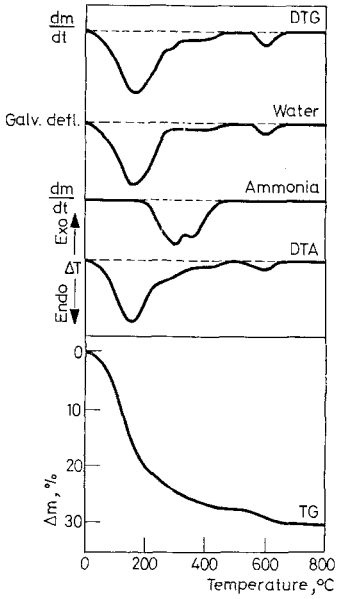

Fig. 1. Thermoanalytical curves of the NH_4Y-zeolite

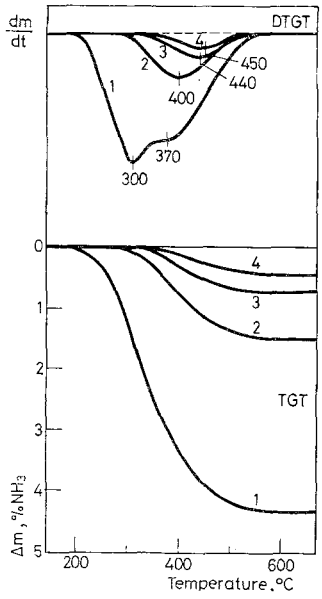

Fig. 2. Titration curves of Y-zeolites. 1 — NH_4Y; 2 — $NH_4LaY_{(1)}$; 3 — $NH_4LaY_{(2)}$; 4 — $NH_4LaY_{(3)}$

Table 1

Amount of ammonia in NH_4Y-zeolite

Sample mass mg	Calcined mass mg	Mequiv. NH_3 / g calcined zeolite	Mean	Deviation from mean %
163.20	113.95	3.541		−1.64
170.22	118.85	3.623		+0.64
153.28	107.02	3.625	3.60	+0.69
158.94	110.97	3.616		+0.44

of repeated cycles. The starting and peak maximum temperatures shifted towards higher values. The peak maximum temperatures are 400, 440 and 450°, respectively.

The ammonia contents of the La^{3+}-exchanged zeolite samples calculated from the titration data, are listed in Table 2.

Table 2

Amounts of ammonia in NH_4LaY-zeolites

$NH_4LaY_{(1)}$			$NH_4LaY_{(2)}$			$NH_4LaY_{(3)}$		
% NH_3	mean	deviation from mean %	% NH_3	mean	deviation from mean %	% NH_3	mean	deviation from mean %
1.44		−2.60	0.720		0.00	0.449		+1.35
1.53	1.48	+3.69	0.697	0.72	−3.18	0.437	0.44	−1.35
1.47		−0.37	0.738		+2.56	0.450		+1.58
1.48		−0.71	0.725		+0.69	0.437		−1.35

The thermogastitrimetric determination of ammonia serves as an indirect way to establish the amount of lanthanum on the zeolite. The amount of lanthanum was calculated using the following equations:

$$100 = m_z + m_{La} + m_{H_2O} + m_{NH_3} \tag{1}$$

$$3.60 = \frac{\frac{m_{NH_3}}{A_{NH_3}} + \frac{3m_{La}}{A_{La}}}{\frac{m_z}{1000}} \tag{2}$$

where

m_z is the percentage of the pure zeolite;
m_{La} is the percentage of lanthanum on the zeolite;
m_{H_2O} is the percentage of water in the sample;
m_{NH_3} is the percentage of ammonia on the zeolite;
A_{NH_3} is the molecular weight of ammonia;
A_{La} is the atomic weight of lanthanum.

The amount of water was obtained from the difference between the TG and TGT curves.

From Eqs (1) and (2) it follows that

$$m_{La} = \frac{100 - m_{H_2O} - m_{NH_3} - \frac{1000\, m_{NH_3}}{3.60\, A_{NH_3}}}{\frac{3000}{3.60\, A_{La}} + 1} \qquad (3)$$

The capacity values obtained with the use of Eqs (1) and (3) are given in Table 3.

Figure 3 shows the increase of lanthanum and the decrease of ammonia in capacity as functions of the number of ion-exchange cycles.

Table 3

Capacity values obtained for NH_4Y and NH_4LaY-zeolites

Sample	Mequiv. NH_3 / g calcined zeolite	Mequiv. La / g calcined zeolite	Total
NH_4Y	3.60	0.00	3.60
$NH_4LaY_{(1)}$	1.32	2.28	3.60
$NH_4LaY_{(2)}$	0.66	2.94	3.60
$NH_4LaY_{(3)}$	0.40	3.20	3.60

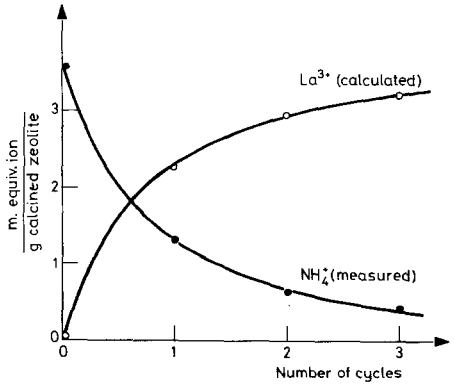

Fig. 3. Changes in capacity of Y-zeolite in the $NH_4^+ \rightarrow La^{3+}$ ion-exchange process

After a three times repeated ion-exchange process 88.9% of the ammonia was replaced by lanthanum.

The amount of lanthanum on the zeolite was determined by X-ray spectrometry.

The amount of water was found to be 26.0 ± 0.2% in each case.

Conclusions

With the use of selective EGA methods combined with derivatograph the thermal decomposition of zeolites can be investigated in detail.

The release rates and the amounts of the individual decomposition products can easily be determined. By continuous monitoring of ammonia in the carrier gas the $NH_4^+ \rightarrow La^{3+}$ ion-exchange process can be followed and the accurate capacity values determined.

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RÉSUMÉ — Des catalyseurs à zéolites de type NH_4Y et NH_4LaY ont été préparés par échange d'ions cyclique d'une zéolite Linde Y synthétique. Le dégagement d'ammoniac et d'eau a été suivi avec un dispositif automatique thermogasotitrimétrique ainsi qu'avec un détecteur d'eau sélectif opérant en continu.

L'échangeabilité des ions NH_4^+ avec La^{3+} sur la zéolite a aussi été étudiée. On a trouvé que la capacité de la zéolite NH_4Y était 3.60 méquiv./g de zéolite calcinée. En répétant trois fois le processus d'échange d'ions, 88.9%. de l'ammoniac ont été remplacés par le lanthane.

ZUSAMMENFASSUNG — Zeolithkatalysatoren vom Typ NH_4Y und NH_4LaY wurden durch zyklischen Ionenaustausch eines synthetischen Linde Y Zeoliths hergestellt. Die Freisetzung von Ammoniak und Wasser wurde durch ein automatisches thermogastitrimetrisches Gerät sowie einen kontinuierlichen selektiven Wasserdetektor verfolgt.

Die Ionenaustauschbarkeit von NH_4^+ gegen La^{3+} an dem Zeolith wurde ebenfalls untersucht. Die Kapazität des NH_4Y Zeoliths wurde für 3.60 mequiv/g kalzinierten Zeolith gefunden. Nach dreimalig wiederholtem Ionenaustauschprozess waren 88.9% des Ammoniaks durch Lanthan ersetzt.

Резюме — Цеолитные катализаторы типа NH_4Y и NH_4LaY были получены циклическим ионным обменом синтетического Y цеолита Линде. Выделение аммиака и воды было прослежено с помощью автоматической термогазометрической приставки, а также с помощью селективного датчика воды непрерывного действия. Была также исследована ионообменная способность NH_4^+ на La^{3+} на цеолите. Найдено, что ионообменность NH_4Y цеолита составляет 3.60 мэкв/г калцинированного цеолита. После трехкратного ионного обмена 88.9% аммиака было замещено лантаном.