THERMOANALYTICAL INVESTIGATIONS ON ION-EXCHANGED Y-ZEOLITES

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NH₄Y and NH₄LaY-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 NH₄⁺ for La³⁺ on the zeolite was also investigated. The capacity of the NH₄Y-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 NH₄Y 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 La³⁺ in the zeolite structure increases their activity and thermal stability in alkylating reactions.

In the present study thermoanalytical investigations were carried out on NH₄Y and NH₄LaY-form zeolites for the continuous and selective monitoring of ammonia and water release and to follow the NH₄⁺ → La³⁺ ion-exchange process.

Experimental

Materials used

Union Carbide LZ-452 type synthetic Y-zeolite with a SiO₂/Al₂O₃ molar ratio of 4.91 was applied. The composition of the zeolite in water-free form was the fol-
In the air-dried form the water content was about 24% and the specific surface area was 902 m²/g.

NH₄Y-form zeolite was prepared by three times repeated ion-exchange of the Linde Y-zeolite with 2.5 M NH₄NO₃ solution.

The NH₄LaY forms were made from the NH₄Y one by stepwise ion-exchange of NH₄⁺ for La³⁺ by treatment with 2.5 M La(NO₃)₃ solution. In this way mixed ammonium-lanthanum forms designated NH₄LaY(1), NH₄LaY(2) and NH₄LaY(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 dm³/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 NH₄Y-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 NH₄Y, NH₄LaY(1), NH₄LaY(2) and NH₄LaY(3) samples are shown in Fig. 2. By comparison of the corresponding curves, the NH₄⁺ → La³⁺ ion-exchange process can be followed as a function of the number.