TEMPERATURE PROGRAMMED DESORPTION OF AMMONIA FROM DEALUMINATED CLINOPTILOLITE

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Ammonia was used for adsorption on calcined dealuminated NH-clinoptilolite. Four acid site types of clinoptilolite were determined by TPD. Extraframework aluminium remained in clinoptilolite structure after dealumination increases the relative number of weak acid sites and has blocking influence on strong acid sites determination.

Key words: clinoptilolite, dealuminated, TPD, DTG, mass spectra

INTRODUCTION

Temperature programmed desorption of probe moleculer is, beside of IR spectroscopy, ^{1}H-MAS-NMR and microcalorimetry a method frequently used for characterization of acid properties of zeolites.

Hegde et al. [1] studied the acidity of zeolite Beta by TPD of ammonia. Only desorption peak in the 653-673 K region was found to correlate with the Al content, acidity and catalytic activity of zeolite. The peak at 823 K is due to dehydroxylation, because no NH_3 was detected in the desorbate, only H_2O was observed.

Lok et al. [2] reported the TPD spectra for ammonia desorption from zeolites Y and L. NH_4-Y exhibited three desorption peaks at 393, 489 and 553 K. Si-enriched NH_4-Y showed two not well resolved NH_3 peaks at 586 and 705 K. The NH_3-TPD of NH_4-L sample showed 3 peaks at 385, 691 and 821 K. The last peak being associated with partial decomposition of the crystal.

Meyers et al. [3] studied the acidity changes of mordenite using TPD-NH_3 methods. The high-temperature peak at 475°C depended on structural aluminium content in mordenite. The amount of NH_3 desorbed at high temperature was taken as a measure of strong acidity.

Auroux et al. [4] combined the TPD and comparative calorimetric studies of H-ZSM5, H-Y and H-Ferrierite for acid sites distribution determination. The weight loss and ΔH of NH_3 desorption was measured at increasing temperature. Three different acid sites were found in all cases, but the peak temperatures and amount of desorbed NH_3 varied at high-temperature peaks from 560 to 720°C and from 138 to 165 KJ/mol, respectivelly.

The aim of present work is to compare the relative acid sites number of natural cation-, NH_4-, dealuminated- and acid washed dealuminated-forms of clinoptilolite and follow up the influence of dealumination degree for single peaks position shift.

EXPERIMENTAL

Material

Rhyolite tuff containing 70 mass % of clinoptilolite was used as a starting material. The sample was treated with 3M NH_4Cl at room temperature and during 3 times 24 hours. Dealumination was carried out by stirring of NH_4-clinoptilolite with 0.75M $(NH_4)_2SiF_6$ at 95°C during 1, 3, 16 and 24 hours. Samples D, D_0, D_1, D_3, D_6 and D_{11} (Table I) were deammoniated and dehydrated at 500°C, in dynamic vacuum (5 Pa) for 5 hours. The probe molecules were sorbed after cooling for 1 hour at 50°C. Then the samples were outgased at 200°C 1 hour to remove physically sorbed probe molecules and studied at thermal analysis.

Acid washing

Dealuminated samples were washed with 1 N HCl at room temperature during 1.5 hour, to remove extraframework (EFAl). The method of acid washing was chosen on the base of condition, that the aluminium loss during the acid treatment must be lower than 5 mass % in the case of starting material.

Probe molecule

NH_3 - liquid NH_3 was saturated by dried KSCN. Trace amount of water was removed by NaA zeolite and the solution was used for sorption at 22±2°C and at the saturated steam pressure.

Methods

Derivatograph Q-1500 (MOM Budapest) was used for DTA, DTG and TG measurements. 560 mg of sample was analysed in air and N_2 at heating rate 20 K/min. DTG curves were fitted using Pitha & Jones computer program [5] for fitting curves to infrared

Table I

Characterization of the dealuminated samples

Sample	Reaction time [h]	Composition	Si/Al ratio
D	0	$Ca_{2.0}Mg_{0.1}Na_{0.6}K_{1.9}Al_{6.7}Si_{29.3}O_{72}$	4.37
D_0	0	$(NH_4)_{6.7}AL_{6.7}SI_{29.3}O_{72}$	4.37
D_1	1	$(NH_4)_{6.03}Al_{6.03}SI_{29.97}O_{72}$	4.97
D_3	3	$(NH_4)_{5.26}Al_{5.26}SI_{30.74}O_{72}$	5.84
D_6	16	$(NH_4)_{4.21}Al_{4.21}SI_{31.79}O_{72}$	7.55
D_{11}	24	$(NH_4)_{4.15}Al_{4.15}Si_{31.85}O_{72}$	7.67

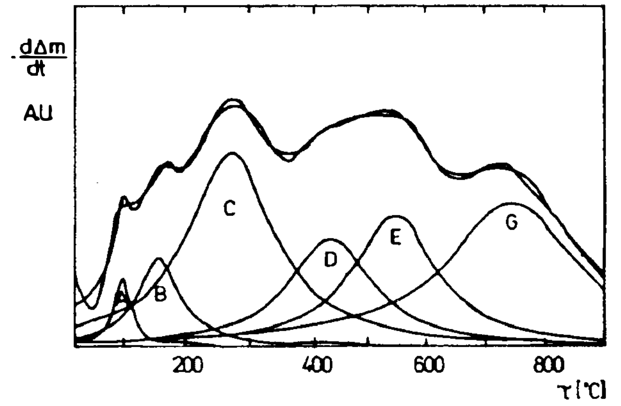

Fig. 1. DTG curve of NH_3 desorption from D_3 sample and fitted desorption peaks.

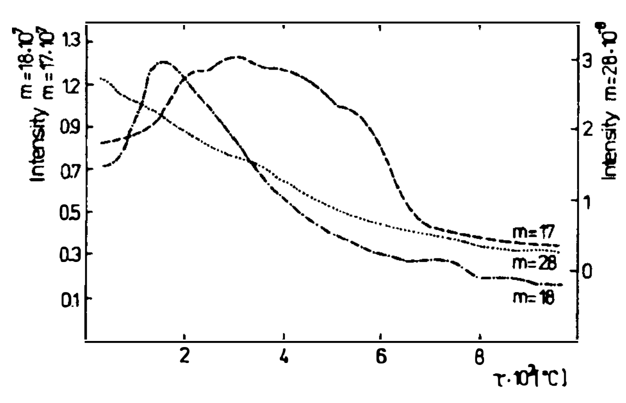

Fig. 2. Mass spectrum of NH_3 desorption from D_3 sample.

band envelope. The relative peak areas were calculated taking into account B-, C-, D- and E-NH_3 peaks (Fig. 1).

Netzsch STA-QMS, system 409 thermal analyser was used for desorption products analysis. Heating rate 10 K/min and flow rate of Ar 80 ml/min were used.

The possibility of DTG and mass spectra comparing was checked by means of comparison NH_3 desorption from clinoptilolite at the atmosphere of air and N_2 (Fig. 5). The slight shift of DTG and DTA peaks to higher temperature was found in the case of N_2 (flow rate of N_2 was 80 ml/min.).

RESULTS AND DISCUSSION

DTG curves of NH_3 desorption from starting cation-, NH- and dealuminated-forms of clinoptilolite are in Fig. 4. The shape changes of desorption curves describe the changes of clinoptilolite acid properties after decationization and dealumination.

Six desorption peaks were fitted in DTG curves of NH_3 desorption. Using program for optimalization of temperatures, intensities and half-width it was achieved good agreement sumary envelope function with experimental DTG curve (Fig. 1).

Desorption peak A-NH_3 (Fig. 1) occurs at 160°C (D_0). The higher content of NH_3 ($m=17$) (m = molecular weight) along with water ($m=18$) was observed in the case of NH_3 desorption (Fig. 2). Curve $m=28$ was scanned in order to check the possibility of desorbed NH_3 oxidation connected with N_2 formation. The overlaping of $m=18$ and $m=17$ curves (Fig. 2) was found below the evacuation temperature (200°C). This phenomenon indicates the possibility of small NH_3 molecules migration in the zeolite porous structure. From present measurement can not be judged the influence of adsorbed water molecules on the NH_3 migration degree in the structure. The desorption maxima of A-NH_3 were shifted from 160 (D_0) to 208°C (D_{11}) with dealumination. The shape simmilarity of D and D_{11} curves (Fig. 4) can be explaned by the same influence of the EFAl and exchangeable starting cations on the water adsorption.

The position of desorption peak B-NH_3 is at 245°C (D_0) (Fig. 1). The position change of B-peak with

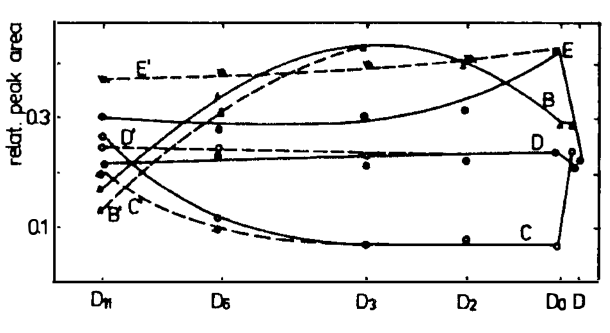

Fig. 3. Dependence of relative peak areas of ammonia desorption on dealumination degree.

dealumination is slightly shifted to higher temperatures. The course of $m=18$ and $m=17$ curves (Fig. 2) indicate the presence of NH_3 and small amount of water at desorption products. Water content at desorption gases is due to moisture adsorption on very weak and unoccupated acid sites and supposed migration of NH_3 and water in zeolite structure. B-NH_3 curve (Fig. 3) shows the dependence of peak B-NH_3 area from aluminium content. The desorbed amount of NH_3 exhibits maximum in D_3 sample. Supposing, that the peak area corresponds to number of acid sites, the relative number of weak acid centers B-NH_3 coincides with the shape of curve B (Fig. 3). The relative number of acid sites B-NH_3 decreases in accordance with B'-NH_3 curve after acid washing. EFAl, retaining at dealuminated samples after washing, is removed by acid treatment. Molecules of ammonia can be bonded onto EFAl because of small kinetic diameter (0.26 nm) and can be bonded at the porous system, partially occupated by EFAl.

The peak positions of C-NH_3 (Fig. 1) were shifted from 370 (D_0) to 350°C (D_{11}) at dealumination. Peak temperature decreasing is connected with partial pore system destruction and mesopore formation. The relative mesopore volume increases with dealumination (6) and the diffusion of probe molecules is easier. The relative number of acid sites C-NH_3 (Fig. 3) increases after dealumination. The number of acid sites after acid washing is evident from C'-NH_3 curve (Fig. 3). We described previously (7) the faster weak acid sites decreasing in comparison with strong acid sites. The C-C'curves for NH_3 refer to probe molecules adsorption on EFAl, the certain amount of which was not removed by acid washing and remained in clinoptilolite structure.

Peak position of D-NH_3 (Fig. 1) is at 480°C (D_0). The shift of peak temperature was found to 448°C (D_{11}) at dealumination. In D-NH_3 desorption gaseous products was only NH_3 detected (Fig. 2). Relative peak area of D-NH_3 (Fig. 3) slightly decreases after dealumination. The number of acid sites slightly increases after acid treatment (Fig. 3). This indicates the blocking influence of EFAl, removable by HCl treatment, for NH_3 adsorption.

Peak E-NH_3 (Fig. 1) has desorption maximum at temperature interval from 593 (D_0) to 569°C (D_{11}). At desorption gaseous products at temperature interval of E-NH_3 (Fig. 1) was identified only ammonia (Fig. 2). Relative area of desorption peaks E corresponding with relative number of strong acid sites

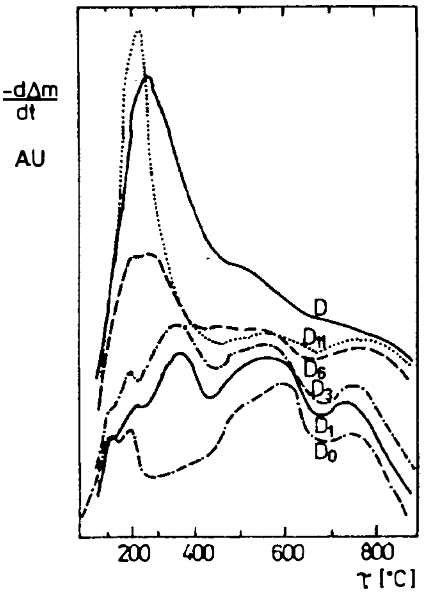

Fig. 4. DTG curves of ammonia desorption for various dealumination degree.

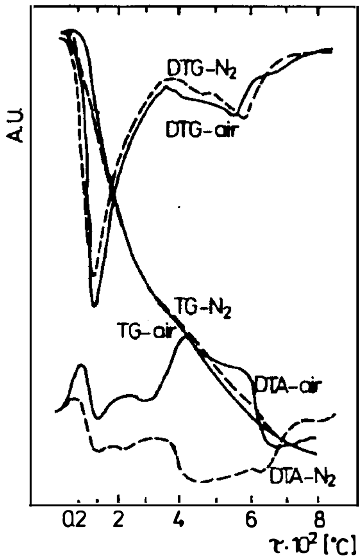

Fig. 5. The comparison of thermal analysis results of NH_3-D_0 sample carried in air and N_2.

decreases with dealumination. the signifficant increasing of amount of desorbed NH_3 was found after acid treatment of dealuminated samples (E'-NH_3) in comparison with E-NH_3. The signifficant influence of acid treatment of dealuminated clinoptilolite can be supposed as a result of accession improving of strong acid centers for sorption of ammonia molecules.

Desorption peaks G-NH_3 (Fig. 1) present the weight loss connected with dehydroxylation of Bronsted acid sites and formation of Lewis acid ones. The presence of water can be found at 730°C (Fig. 2) at desorption products.

NH_3 seems convenient for clinoptilolite acid sites determination because of small kinetic diameter (0.26nm) and desorption without decomposition. there is the possibility of partial NH_3 molecules redistribution in the case of weak acid sites.

CONCLUSION

The adsorption of ammonia with subsequent temperature programmed desorption give the possibilities to test the acid sites of dealuminated zeolites. There are two consequences of dealumination:

i) The EFA1 remained in zeolite structure is the product of izomorphous substitution, increases the weak acid sites determination by NH_3-TPD and is the cause of the shift of A, B-peak position to higher temperature. Acid washing decreases the weak acid sites peak areas and increases the strong ones as the result of EFA1 removing.

ii) The dissolution-degradation is the by-process of izomorphous substitution, the results of which is mesopore formation and the shift of C, D, E peaks position to lower temperature.

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ŠTÚDIUM TEPLOTNE PROGRAMOVANEJ DESORPCIE NH_3 Z DEALUMINOVANÉHO KLINOPTILOLITU POMOCOU DTG A HMOTNOSTNÝCH SPEKTIER

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Ryolitický tuf s obsahom klinoptilolitu 70% bol dealuminovaný vodným roztokom $(NH_4)_2SiF_6$. NH_3 bol adsorbovaný na deamonizovaný a dehydratovaný povrch kalcinovaných vzoriek zeolitu. Metódou teplotne programovanej desorpcie boli rozlíšené 4 typy kyslých centier. Realítny počet kyslých centier je funkciou stupňa dealuminácie a je závislý aj na použití kyslého preplachu dealuminovaných vzoriek. Kyslým preplachom sa odstraňuje mimoštruktúrny hliník, vytvorený dealumináciou, ktorý má blokujúci vplyv na stanovenie počtu silných kyslých centier.

Obr. 1: DTG krivka desorpcie NH_3 zo vzorky D_3 a fitované desorpčné píky.

Obr. 2: Hmotnostné spektrá desorpcie NH_3 zo vzorky D_3.

Obr. 3: Závislosť realitnej plochy píkov desorpcie NH_3 od stupňa dealuminácie.

Obr. 4: DTG krivky desorpcie NH_3 pre rôzne stupne dealuminácie.

Obr. 5: Porovnanie výsledkov termickej analýzy vzorky NH_3-D_0 vo vzduchu a v dusíku.