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METHODS FOR CHARACTERIZATION AND THEIR INFLUENCE ON THE STRUCTURE OF SILICON-RICH ZEOLITES

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H, Li, Na, Cs, NH_4, Mg and Al–ZSM 5 zeolites and H and NH_4-mordenites were studied by DTA, X-ray diffraction, TPD and adsorption measurements. The stability relating to dealumination and structure destruction depends on the nature of the cation.

H and NH_4–ZSM 5 were strongly dealuminated to silicalitelike phases in the temperature range 973–1273 K during the course of the DTA measurement. NH_4-mordenite was dealuminated below 873 K in the TPD experiment on the deammonization.

The thermal destruction of ZSM 5 containing Na^+, Mg^{2+}, Al^{3+} and Cs^+ ions begins at about 1400 K. Excess sodium ions present in the original Na–ZSM 5 decreased the thermal stability. For H and NH_4-mordenites, complete amorphization was found at 1270 K.

The catalytic properties of ZSM 5 can be modified by ion-exchange. In this paper, data on the thermal stability, the acid sites and the pore volume are presented for ZSM 5 zeolites containing different metal ions.

Experimental

Sample preparation

The samples are listed in Table 1. From commercial Na–ZSM 5 (sample 6: HS–30, VEB CK Bitterfeld), samples 4, 5 and 7–9 were prepared by ion-exchange in 0.1 *N* salt solution. Sample 10 was obtained by treatment with HNO_3. The dealumination of sample 4 lead to samples 1–3. The parent sample 6 was further modified by washing to eliminate the excess sodium, and a second Na–ZSM 5 zeolite was prepared by Na^+-exchange of sample 4 (Table 2).

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Table 1 Composition of the samples and TPD results

Sample	Al/u.c.	Cation		TPD peak area, mmol/g	
		degree of exchange, %	radius, Å	520 K	720 K
1 HZSM 5	4.9	100		1.25	0.6
2 HZSM 5	1.5	100			
3 HZSM 5	0.8	100			
4 NH_4ZSM 5	5.4	100	1.43	0.65	
5 LiZSM 5	5.4	*	0.60	1.18	0.14
6 NaZSM 5	5.4	100	0.95	0.74	
7 CsZSM 5	5.4	*	1.69	0	
8 MgZSM 5	5.4	66	0.65	1.11	0.31
9 AlZSM 5	5.4	66	0.50	1.0	0.32
10 HZSM 5	5.4	100			
11 modernite					
H^+ form	3.0	100			
NH_4^+ form	6.4	100			

* probably 100%.

Instrumental

Thermal analysis: an STA 429 Netzsch Gerätebau GmbH, FRG; dried N_2 70 ml min^{-1}, 5–10 deg min^{-1}, 30–50 mg, and a MOM derivatograph, Budapest, Hungary, 5 deg min^{-1}, 170 mg; TPD of NH_3: 12 and 4 deg min^{-1}, a stream of He, a thermal conductivity detector; X-ray: a Guinier-type camera, CuK_α radiation.

Results and discussion

Thermal analysis and X-ray

H–ZSM 5 did not show any marked effect in the DTA curves (Fig. 1) on heating to 1273 K. However, X-ray investigations revealed that strong dealumination occurs and silicate-like samples are formed (Table 2). The dealumination is also confirmed by the reduction in the uptake of water [1].

Between 1370 and 1570 K, a very weak exothermic deviation from the base line is observed, which corresponds to the collapse of the zeolitic structure. The amorphous material crystallized at about 1690 K to α-cristobalite, as indicated by an exothermic peak in the DTA curve.

Of the ZSM 5 samples containing different cations, the original Na–ZSM 5 shows

Table 2 X-ray and DTA results

Sample	Treatment, K	Products	DTA, exothermic
1 HZSM 5	1273	ZSM 5 dealuminated	1170–1440 weak
	1610	α-, β-cristobalite, amorph.	1682 Tp*
	1700	α-, β-cristobalite	
10 HZSM 5	as 1	as 1	1170–1520 weak 1665 Tp
2 HZSM 5	1273	ZSM 5 dealuminated	
3 HZSM 5	1273	ZSM 5 dealuminated	
6 NaZSM 5 original	1170	residual ZSM 5, amorphous	
	1273	α-quartz, α-cristobalite β-cristobalite-like (tetragonal)	1290 Tp
	1540	α-, β-cristobalite-like $Na_6Al_4Si_4O_7$	> 1540 sintering
	1720	α-, β-cristobalite-like	
NaZSM 5 washed	1273	mainly ZSM 5	> 1375 sintering
NaZSM 5 exchang.	1273	ZSM 5	> 1420 sintering
7 CsZSM 5	1273	ZSM 5	
	1473	residual ZSM 5	> 1490 sintering
	1718	residual ZSM 5, β-cristob.	
8 MgZSM 5	1273	ZSM 5	
	1423	residual ZSM 5, β-cristob.	1465 Tp
	1573	α-, β-cristobalite	
9 AlZSM 5	1273	ZSM 5	
	1458	residual ZSM 5, β-cristob.	> 1477 sintering
	1720	α-, β-cristobalite	
11 H-mordenite	1273	amorphous	1280 Tp
	1573	mullite, α-cristobalite	1470 Tp
	1700	mullite, α-, β-cristobal.	> 1620 sintering

* Tp = temperature of the peak maximum.

the lowest thermal stability. A partial structural destruction was already observed at 1170 K. A sharp exothermic peak at 1290 K marked the complete transformation into α- and β-cristobalite. Since the thermal stability increases after washing of the sample, the relative instability is due to the excess of sodium in this sample (Na/Al = 1.13).

The thermal desctruction of ZSM 5 containing Mg^{2+}, Al^{3+} and CS^+ ions (transformation into α- and β-cristobalite) begins at about 1400 K.

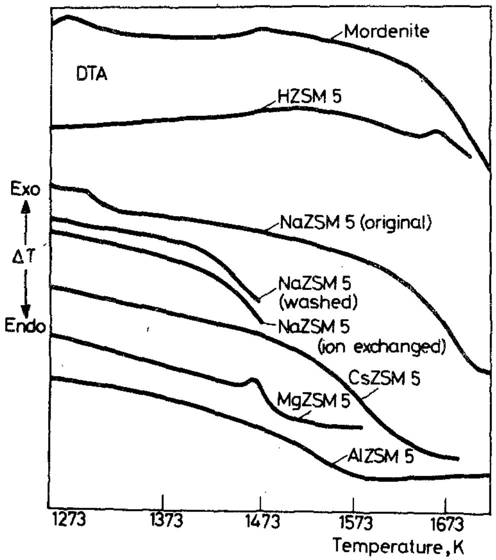

Fig. 1 DTA curves on HZSM 5, cation exchanged ZSM 5 and mordenite

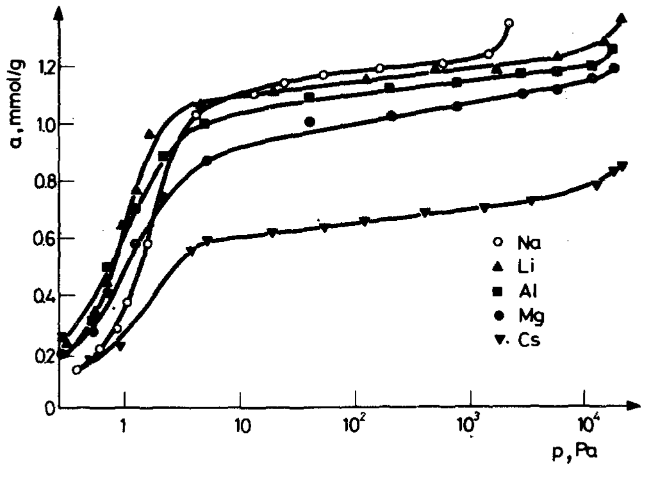

Fig. 2 Adsorption isotherms of *n*-hexane on cation exchanged ZSM 5

For mordenite, a weak exothermic peak is found at 1270–1280 K in the DTA. The X-ray investigation revealed the complete amorphization of the sample. A further exothermic peak (1470 K) and sintering (above 1560 K) mark the formation of mullite and small amounts of α-cristobalite, respectively. Above 1700 K, β-cristobalite too is formed.

Adsorption isotherms

Adsorption isotherms of *n*-hexane on ZSM 5 exchanged with Li^+, Na^+, Cs^+, Mg^{2+} and Al^{3+} are given in Fig. 2. the adsorption capacity of 1.2 mmol g^{-1} (0.16 cm^3 g^{-1}) lies in the range of the usual values. In the case of Cs–ZSM 5, only half of this value is found. The large Cs^+ ion probably blocks part of the channel system in the ZSM 5 structure [2].

Temperature-programmed NH_3 desorption

In agreement with the literature [3], the TPD curves of H–ZSM 5 show two maxima (at about 520 and 720 K; Fig. 3). In the thermal decomposition of NH_4–ZSM 5, a unique peak at 720 K corresponds to the chemisorption of NH_3 on Brönsted acid sites [1]. The TPD curves of H–ZSM 5 are completely reproducible in repeated runs, i.e. no changes are detectable.

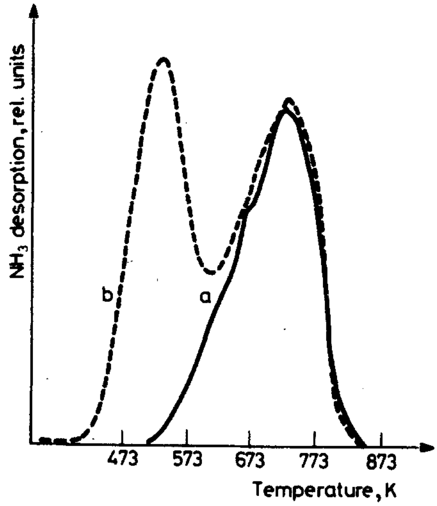

Fig. 3 TPD of NH_3 on ZSM 5

a) thermal decomposition of NH_4ZSM 5 to HZSM 5*

b) NH_3 desorption on HZSM 5/NH_4ZSM 5

(adsorption at 390 K, heating rate 12 deg min^{-1}, 100 mg)

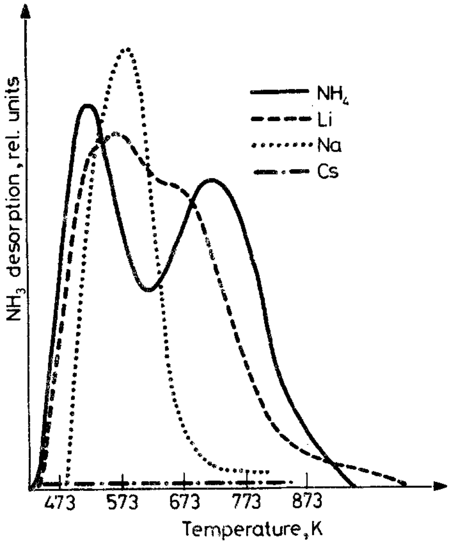

Fig. 4 TPD of NH_3 on cation exchanged ZSM 5 (Conditions as in Figure 3b),

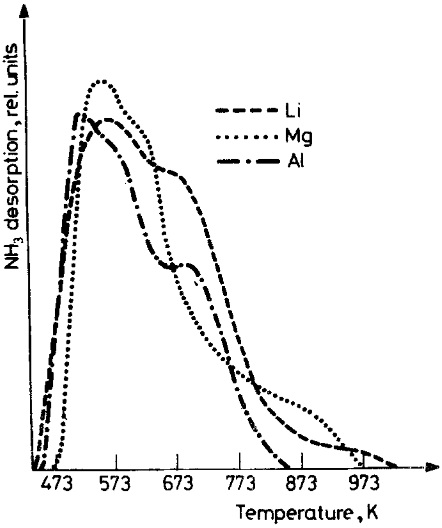

Fig. 5 TPD of NH_3 on cation exchanged ZSM 5

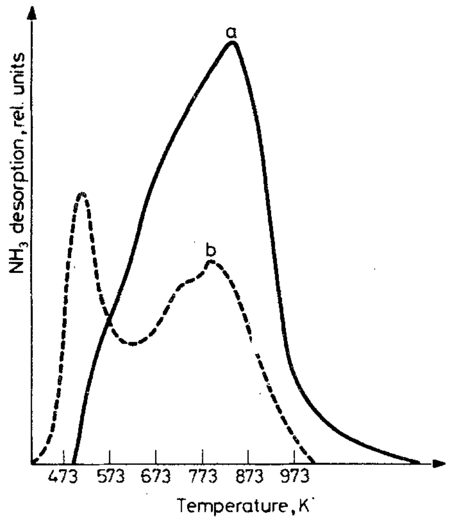

Fig. 6 TPD of NH_3 on mordenite
a) thermal decomposition of NH_4 mordenite to H mordenite
b) NH_3 desorption on H mordenite (conditions as in Figure 3b)

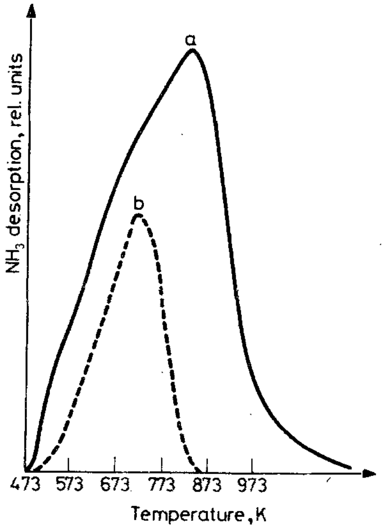

Fig. 7 Comparison of the thermal decomposition of NH_4-mordenite (a) and NH_4ZSM 5 (b)

The 520 K peak reflects the interaction of NH_3 with centres weaker than the zeolitic cations. The influence of the radius and charge of the cation is demonstrated in Figs 4 and 5 and in Table 1. In the alkali metal series, the peak area decreases with increasing cation radius, in accordance with the results reported by Derewinski et al. [4].

In contrast to H-ZSM 5, mordenite is already changed during the thermal decomposition of the NH_4^+ form. Figure 6 demonstrates the reduction of the high-temperature peak due to dealumination. The broader distribution of the acid strength for mordenite as compared with ZSM 5 follows from Figs 7 and 8 [5].

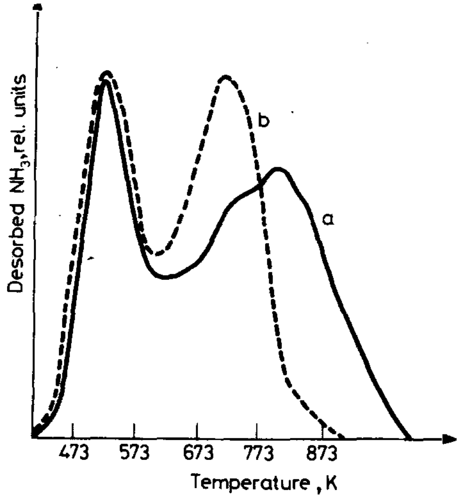

Fig. 8 Comparison of NH_3 TPD on H-mordenite (a) and HZSM 5 (b)

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Zusammenfassung — H-, Li-, Na-, Cs-, NH_4-, Mg- und Al-Zeolithe ZSM 5 sowie H- und NH_4-Mordenit wurden durch DTA, Röntgenbeugung, temperaturprogrammierte Desorption (TPD) und Adsorptionsmessungen untersucht. Die Stabilität gegenüber Dealuminierung und Strukturzusammenbruch hängt von der Art des Kations ab. H- und NH_4-ZSM 5 werden im Verlauf der DTA-Messungen im Bereich 973—1273 K zu Silicalit-ähnlichen Phasen dealuminiert. NH_4-Mordenit wird unterhalb 873 K bei der Ammoniakabspaltung im TPD-Experiment dealuminiert. Der thermische Zusammenbruch von Na-, Mg-, Al- und Cs-ZSM 5 beginnt um 1400 K. Im ursprünglichen NaZSM 5 vorhandene überschüssige Natriumionen verringern seine thermische Stabilität. Für H- und NH_4-Mordenit wird bei 1270 K vollständige Amorphisierung gefunden.

Резюме — Методами ДТА, рентгенофазового анализа и адсорбции изучены H, Li, Na, Cs, NH_4, Mg, Al ZSM 5 цеолиты и H-, NH_4-мордениты. Устойчивость к деалюминированнию и характер деструкции зависят от типа катиона. Методом ДТА установлено, что образцы H- и NH_4—ZSM 5 в интервале температур 973—1273 подвергаются интенсивному деалюминированию с образованием силикатоподобных фаз. При проведении ТПД экспериментов установлено, что NH_4-морденит деалюминируется ниже температуры 873 К. Термическая деструкция образцов ZSM 5 цеолитов, содержащих ионы натрия, цезия, магния и алюминия, начинается при температуре около 1400 К. Наличие избыточных ионов натрия в исходном образце цеолита NaZSM 5 уменьшает его термоустойчивость. Полная аморфизация H/NH_4-морденита происходит при 1270 К.