

TEMPERATURE-PROGRAMMED DESORPTION (TPD) OF AMMONIA FROM THE H FORM OF A MORDENITE AFTER DIFFERENT PRETREATMENT TEMPERATURES

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Temperature-programmed desorption of ammonia from the H form of a mordenite was carried out after pretreatment at different temperatures. It could be shown that a quantitative registration of the acidic OH groups is possible. Moreover, from the desorption curves, information is obtained about the alteration of the acidic properties as a function of the temperature of pretreatment.

H mordenites are frequently used as catalysts because of their porous structure, acidity and thermal stability [1, 2]. In order to characterize the number, nature and strength of the acidic sites of zeolites, NH_3 can be used as a suitable probe molecule. For this, temperature-programmed desorption (TPD) is a suitable method [2–13], besides the microcalorimetric estimation of adsorption heats [14–19] and other methods [20–23]. In this connection, many papers report the change in NH_3 desorption depending on the Si/Al ratio, and also the dealumination of H mordenites [2, 8–10]. The acidic properties of H mordenites after exchange with K^+ ions [8], or after treatment with $\text{Si}(\text{OCH}_3)_4$ [11], are also characterized by this method. However, only limited information is available about the changes in the TPD curves of ammonia after pretreatment at different temperatures. Thus, in the present paper the influence of the temperature of pretreatment of H mordenite on the TPD of ammonia is investigated systematically, because it is known that the adsorption behaviour of ammonia is changed significantly by reason of the partial dehydroxylation of the zeolite.

Experimental

All investigations were carried out in a conventional flow apparatus. Desorption products were recorded with a heat conductivity detector (H_2O and NH_3) and a

flame ionization detector (NH_3). The NH_4 form of the mordenite was obtained by a four times repeated ion-exchange, using a solution of $\text{NH}_4\text{NO}_3/\text{NH}_4\text{OH}$ at 363 K ($\text{Na}_{1.2}(\text{NH}_4)_{6.8}\text{Al}_8\text{Si}_{40}\text{O}_{96}$). For each experiment, 0.2 g of zeolite was diluted with 1 g of quartz of equal grain size (0.2–0.4 mm), then heated under helium (flow rate 3 l/h) up to a temperature between 673 and 1073 K, and held at the end temperature for 45 min. Ammonia was next adsorbed at different temperatures from a stream of 5 vol. % ammonia in helium for 30 min at a flow rate of 3 l/h, followed by a 45-min flush with pure helium at the adsorption temperature. TPD was then carried out under helium (3 l/h), using a heating rate of 10 deg/min from the temperature of adsorption up to 1073 K. The whole amount of ammonia desorbed was estimated additionally by absorption in 0.05 M H_2SO_4 and back-titration with KOH.

Results and discussion

In Fig. 1 curve 1, the signal of the heat conductivity detector is shown for the thermal activation of the NH_4 form of the mordenite. The peak up to about 523 K corresponds to the dehydration of the zeolite. From 523 K up to about 973 K, deammoniation occurs, and then, beginning at about 773 K, dehydroxylation [24, 25]. Figure 1 also shows the TPD curve of NH_3 after adsorption at 523 K for the zeolite pretreated at 673 K. Both the peak maximum temperature and the shape of the desorption curve are in good agreement with those of the original deammoniation. The NH_3 amount desorbed in the range from 573 K to 973 K (2.51 ± 0.25 mmol/g) is a little greater than the theoretical number of H^+ centres on the zeolite (2.34 mmol/g). Mirodatos et al. [12] and Schweckendiek [13] also found that the NH_3 amount which corresponds to the whole H^+ content is desorbed in a relatively uniform peak.

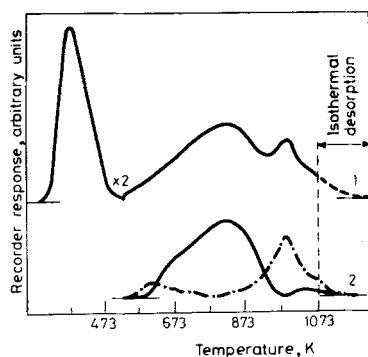


Fig. 1 1: Thermal activation of NH_4 mordenite (recorder response of heat conductivity detector; 2: TPD curves after adsorption of NH_3 at 523 K, — NH_3 , - - - H_2O)

Figure 2 shows TPD curves for different amounts of NH_3 . After adsorption at 373 K (curve 1), a further peak results at lower temperatures [7–10, 12]. By combining TPD and FT IR spectroscopy, Lok et al. [7] could show that this peak does not represent the interaction of ammonia with the OH groups of the zeolite. When adsorption is carried out at temperatures above 523 K (curve 3), the shoulder at about 673 K disappears, but the residual course of desorption is comparable to that after adsorption at 523 K (curve 2).

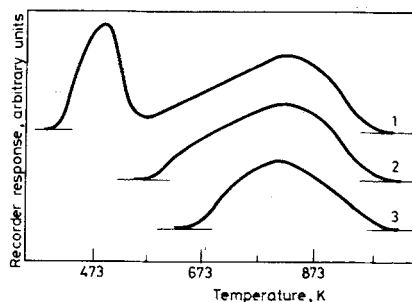


Fig. 2 TPD curves of NH_3 after adsorption of different amounts of ammonia. 1: 3.52 mmol/g, 2: 2.51 mmol/g, 3: 1.92 mmol/g

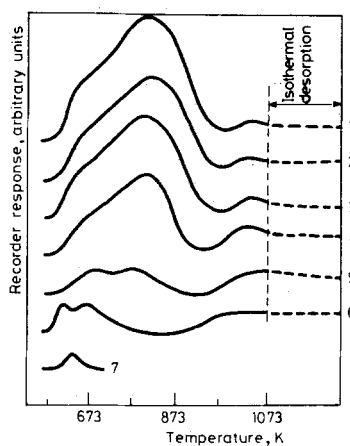


Fig. 3 TPD curves of NH_3 after different pretreatment temperatures (adsorption temperature 523 K). 1: 673 K, 2: 773 K, 3: 823 K, 4: 873 K, 5: 973 K, 6: 1073 K, 7: Na mordenite

Figure 3 shows desorption curves obtained after NH_3 adsorption at 523 K for the mordenite pretreated at different temperatures. It can be seen clearly that the amount of NH_3 desorbed up to 973 K strongly decreases when the pretreatment temperature increases. Moreover, since the Na mordenite desorbs only a very low

amount of NH_3 at lower temperatures under equal adsorption conditions (curve 7), this peak can be assigned to the desorption of ammonia from the acidic OH groups of the zeolite (except for the amount of NH_3 at 673 K) [7, 13]. The shoulder at about 673 K, assigned to the desorption of coordinately bound NH_3 [13], does not disappear; it is visible as a peak after pretreatment at 973 K. Thus, the point here could be that desorption occurs from Lewis acid sites formed previously during deammoniation of the NH_4 form [26], or during preparation of the zeolite.

If the amount of ammonia desorbed up to 973 K is corrected by the amount desorbed after pretreatment at 1073 K, the number of acidic OH groups resulting from the corresponding pretreatment is obtained. This agrees well with the number of OH groups calculated from the amount of water relating to the dehydroxylation peak (see Fig. 4).

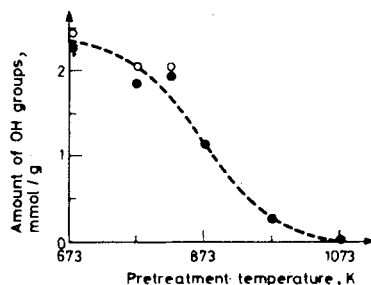


Fig. 4 Number of acidic OH groups as a function of temperature of pretreatment. ● calculated from amount of ammonia desorbed, ○ calculated from amount of water desorbed (dehydroxylation peak)

It is also typical of the course of desorption that the amount of NH_3 desorbed above 973 K (or at higher pretreatment temperatures from about 900 K) increases in parallel with the elevation of the pretreatment temperature. Desorption from strong Lewis acid centres obviously occurs here, these centres being formed by the dehydroxylation of the zeolite. Such a strong interaction of ammonia with Lewis acid sites is explained in the literature in the sense of a dissociative mechanism of chemisorption [19]. A quantitative evaluation of this peak, which is relatively broad and flat, involves large uncertainties, because the desorption is still not finished above 1073 K. Moreover, the splitting of NH_3 at such high temperatures cannot be excluded completely.

After pretreatment at 1073 K, an additional, but small amount of ammonia is desorbed at about 600 K, also resulting from a desorption from Lewis acid sites, because microcalorimetric measurements of NH_3 adsorption showed that in the course of dehydroxylation Lewis acid centres can also be formed where ammonia is bound less strongly than on acidic OH groups [18].

In order to compare the acid strengths of H zeolites of different structures and of different Si/Al ratios by means of the TPD of ammonia, the temperature of the maximum of the desorption curve is used in the literature [8, 9]. This is realistic only if the same model can be used for the description of the kinetics of the desorption process. However, in the case of HY and HZSM-5 zeolites, it could be shown that a satisfactory description of the course of desorption is possible only by means of different kinetic models [27, 28]. Because of the distinct difference between the shapes of the desorption curves of H mordenite and of HY and HZSM-5 zeolites [7-10], the higher peak maximum temperature in the case of H mordenite under comparable experimental conditions cannot be valid evidence of a higher acidity of the mordenite. A kinetic evaluation of ammonia desorption from H mordenite will be dealt with in a later paper.

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Zusammenfassung — Es wurde die Temperatur-Programmierte Desorption von Ammoniak an der H-Form eines Mordenits nach Vorbehandlung bei unterschiedlichen Temperaturen untersucht. Es konnte gezeigt werden, daß damit eine quantitative Erfassung der Anzahl der sauren OH-Gruppen möglich ist. Außerdem erhält man aus den Desorptionskurven Hinweise über die Veränderung der sauren Eigenschaften in Abhängigkeit von der Vorbehandlungstemperatur.

Резюме — Иучена температурно-программная десорбция аммиака на H-форме морденита, предварительно обработанного при различных температурах. Показана возможность количественного определения кислотных OH групп. Кроме того, данные полученные на основе кривых десорбции указывают на изменение кислотных свойств морденита в зависимости от температуры его обработки.