

Measurement of the Acidity of Various Zeolites by Temperature-Programmed Desorption of Ammonia

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The acidity of H-form zeolites which include mordenite, ZSM-5, Y-faujasite, and those modified by cation exchange or dealumination was measured by temperature-programmed desorption (TPD) of NH₃. Ammonia was adsorbed at 373 K to eliminate the contribution of very weak acid sites and improve the spectrum resolution. TPD spectra of mordenites and ZSM-5 zeolites had two desorption peaks named *l* and *h* with peak maximum at around 420 and 680 K, respectively, while the spectra of Y-zeolites had a broad peak. From the peak maximum temperature of *h*-peak, the acid strength was found to be in the order of HM > HZSM-5 > HY. Acid amount was evaluated from the desorption amount of NH₃, and correlated with the infrared intensity of the OH band at 3600 cm⁻¹ and the ammonium band at 1447 cm⁻¹, thus indicating that the amount as well as distribution of strength of Brønsted acid sites can be measured by the present method. Cation exchange poisoned the strong acid sites preferentially, whereas dealumination reduced the acid sites in the whole region.

INTRODUCTION

Acidity is one of the important characteristics of zeolites which make it catalytically effective (1). Recently, eminent interesting catalytic activities of HZSM-5 zeolite have been reported (2). Although much attention has been paid to the role of its pore structure, its acid property may also be a significant factor. To investigate the strength, amount and structure of acid sites in zeolites, one can utilize various methods of acidity measurements such as titration, calorimetry, and infrared spectroscopy. All these have advantages as a method to measure the acidity quantitatively and qualitatively. The restriction which has been encountered concerns the size of base molecules as well as its strength. From such a viewpoint, microcalorimetry by the differential adsorption of ammonia may be fairly satisfactory disregarding its time-con-

suming factor (3, 4). Temperature-programmed desorption of ammonia has also been reported on various kinds of zeolite (5-11). It is considered to be a potential method to know the amount and distribution of acid sites. However, much depends on the experimental conditions such as rate of temperature increment and equilibrium temperature, which make the comparison difficult. Therefore, the purpose of the present study is to obtain TPD spectra of NH₃ systematically on various zeolites. Furthermore, the acidity modified by cation exchange and dealumination is subject to the measurement, since these modifications would bring about the specific acid site distribution by exchanging preferentially with Site I (12) or eliminating primarily with aluminum of some proposed structures (13).

EXPERIMENTAL METHOD

Material. Decationized H-mordenite referred to as HM was obtained from Norton Company, 100-H, and tested to be free from Na cations.

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HY zeolite was prepared from NaY (Linde SK-40). NaY was exchanged using the conventional procedure with an aqueous solution of NH_4Cl at 368 K for 6 h, washed until no Cl^- was detected, dried at 373 K overnight and calcined at 673 K for 2 h. This procedure was repeated four times and HY with only a trace of Na ions was obtained. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio obtained was 6.3, since a portion of aluminum was extracted during the preparation.

NH_4NaY (Na, 17%) was obtained from Union Carbide, Linde Division (Sk-41), and used without further treatment.

A series of ZSM-5 zeolite with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio was prepared according to (14). The materials were converted into hydrogen form by treating with an aqueous solution of NH_4Cl at 373 K.

HM was dealuminated by refluxing in a flask of aqueous HCl at 373 K according to the method described by Eberly, Jr., *et al.* (15). Extraction time (1 to 24 h) and acid concentration (1 to 8 N) were varied to obtain various ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in the dealuminated HM (termed DM) was determined by X-ray fluorescence spectrometry, and is given in parenthesis beside the catalyst symbol, e.g., DM(71). The inherent $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of HM, 13.6, was enhanced up to 71.4 at most.

The zeolites were partially ion-exchanged according to the method previously described (16). The materials were potassium acetate, calcium chloride, and rubidium chloride for K, Ca, and Rb, respectively. The degree of cation exchange was determined by atomic absorption spectroscopy, and is given in parenthesis next to the cation, e.g., K(53)HM. All the catalysts used as starting material were pelleted without a binder, crushed and sized to 28–48 mesh before ion exchange or dealumination.

Temperature-programmed desorption. TPD spectra were measured with a conventional TPD apparatus. In the apparatus, the detection of desorbed molecules was done by the thermal conductivity detector.

About 0.5 g of sample was evacuated in a quartz cell at 773 K for 1 h, exposed to ammonia which was used as a probe base at 373 K for 45 min at the equilibrium pressure of 7.3 kPa, and then evacuated at 373 K for 45 min. TPD measurement was done from 373 to 773 K with a heating rate of $2.5 \text{ K} \cdot \text{min}^{-1}$ and with helium as carrier gas having a flow rate of $60 \text{ cm}^3 \cdot \text{min}^{-1}$.

Infrared spectroscopy. Infrared spectra were recorded on a Jasco IR-G spectrometer working from 4000 to 1200 cm^{-1} . An infrared cell which allowed the sample to be heated at controlled temperature *in situ* was connected to a conventional high vacuum system. About 15 mg of powder were compressed into a disc of 20 mm in diameter and about 3.5 mg/cm^2 thick. The sample disc was evacuated at 743 K of 1 h, and the spectrum was measured at room temperature. For the measurement of ammonia adsorbed, ammonia was adsorbed at room temperature at the equilibrium pressure of 3.5 kPa, and subsequently evacuated at higher temperatures.

Intensity of OH and NH_4^+ bands was quantitatively measured to know the relative concentrations by using

Concentration of OH or

$$\text{NH}_4^+ \propto \frac{1}{W} \log \frac{I_0}{I},$$

where W , I_0 , and I denote sample weight, transmittance of background, and that of the subject absorption band, respectively.

RESULTS

Temperature-Programmed Desorption

Typical TPD spectra of NH_3 on HM, KHM, and DM are shown in Figs. 1 and 2. Spectra exhibited a fairly good resolution of two peaks named *l* and *h* peaks whose temperatures at peak maximum (T_M) on HM were about 420 and 680 K, respectively. The amounts of NH_3 desorbed from these mordenites and the maximum temperatures are summarized in Table 1.

When ammonia was admitted at room

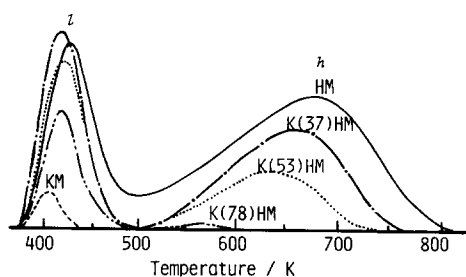


FIG. 1. TPD spectra of NH_3 from HM and KHM.

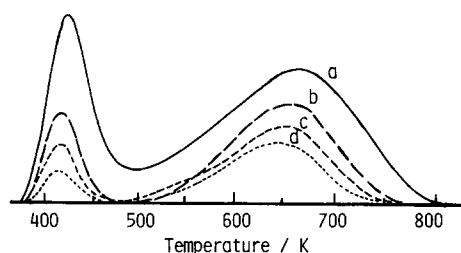


FIG. 2. TPD spectra of NH_3 from DM: (a) HM for comparison; (b) DM(27); (c) DM(36); (d) DM(71).

temperature, and allowed to be desorbed in the TPD experiment, one more desorption peak of NH_3 was observed at a temperature lower than 373 K. It has already been reported that three peaks are observed in the TPD of NH_3 from ZSM-5 zeolite (6). The most weakly adsorbed ammonia is however

out of the scope of the present study, since the weakest acid site is believed to play little role in the usual catalytic reaction.

Further heating of the temperature above 800 K gave another broad peak around 950 K. However, this peak was ascribed to the dehydroxylation of mordenite, because it

TABLE 1
Amount of Desorbed Ammonia and Temperature of Peak Maximum (T_M)

	Amount of desorbed NH_3 (mmol/g-cat.)				Reported	Ref.
	<i>l</i> -Peak T_M (K)	<i>h</i> -Peak T_M (K)	Total	>573 K ^a		
HM	0.41 (426)	0.87 (681)	1.28	0.75	1.24	(3)
K(37)HM	0.34 (418)	0.44 (666)	0.78	0.41		
K(53)HM	0.30 (414)	0.24 (635)	0.54	0.21		
K(78)HM	0.18 (409)	0.01 (567)	0.19	tr		
KM	0.04 (396)	0.0	0.04	0.0		
Ca(24)HM	0.54 (425)	0.87 (681)	1.41	0.80		
DM(27)	0.12 (419)	0.43 (677)	0.55	0.41		
DM(36)	0.10 (416)	0.40 (670)	0.50	0.33		
DM(66)	0.04 (408)	0.28 (650)	0.32	0.27		
DM(71)	0.06 (409)	0.31 (647)	0.37	0.28		
K(68)DM(27)	0.06 (411)	0.24 (630)	0.30	0.13		
HZSM-5(38)	0.23 (428)	0.48 (612)	0.71	0.36	0.40	(3)
HZSM-5(56)	0.09 (420)	0.20 (597)	0.29	0.12		
HZSM-5(103)	0.09 (428)	0.16 (609)	0.25	0.11		
K(63)HZSM-5(56)	0.05 (412)	tr	0.05	0.0		
HY	0.34 (435)	—	1.12	0.26		
Na(17)HY	0.79 (446)	—	2.84	0.29	2.92	(3)
					2.7	(20)
					3.5	(21)
					2.4	(22)
K(25)HY	0.34 (435)	—	0.81	0.07		
Rb(25)HY	0.28 (433)	—	0.66	0.06		

^a The amount of ammonia which is desorbed above 573 K will be used as a criterion on the acidity influencing the methanol conversion (23).

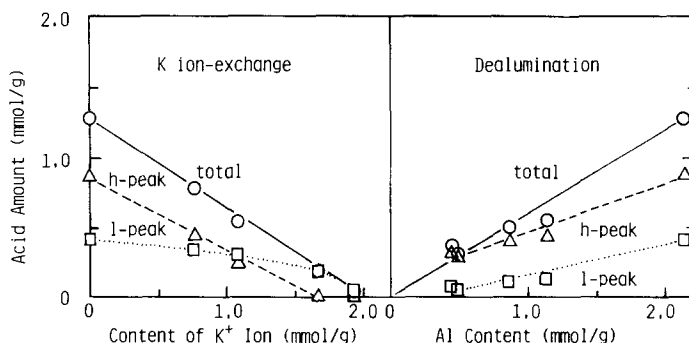


FIG. 3. Change of distribution of acid sites on HM modified by K^+ ion exchange or dealumination. Acid amount of *l*- and *h*-peaks and their total amount are plotted against K^+ ion and aluminum content in KHM and DM, respectively.

was observed without the admission of ammonia.

The amount of desorbed ammonia decreased with the degree of cation exchange or dealumination. In the case of KHM, the *h*-peak decreased prior to the *l*-peak, while dealumination of HM reduced both peaks almost simultaneously. Figure 3 shows these different acidity profiles, in which the acid amounts are plotted against the K^+ cation and aluminum content in KHM and DM, respectively.

T_M of *h*-peaks decreased gradually with increasing K-cation exchange level. In other words, not only the amount of acidity but also its distribution were modified by K-exchange. On the other hand, the maximum temperatures on various DM remained almost constant.

The total amount of NH_3 desorbed from HM, 1.28 mmol/g, was about 60% of the aluminum content of HM matrix. Remaining 40% of Al cation may contribute to the formation of acid sites which are so weak as to liberate NH_3 at temperatures lower than 373 K, because the ratio of the amount of ammonia adsorbed at room temperature to the aluminum content has been reported to be close to 1 on ZSM-5 and dealuminated HY (9).

On K-cation exchanged DM, another desorption peak was observed between *l* and *h* peaks (Fig. 4).

TPD spectra were obtained on other

types of zeolite such as ZSM-5 (Fig. 5) and HY zeolite (Fig. 6). HZSM-5 exhibited two peaks at 420 and 597 K, independent of its SiO_2 to Al_2O_3 ratio, similar to HM and DM. The spectrum was basically in agreement with those reported by Topsøe *et al.* (6) except for the peak below 373 K. As with the case of mordenite, the cation exchange of HZSM-5 resulted in the preferential decrease of *h*-peak rather than *l*-peak, since the K(63)HZSM-5(56) had only an *l*-peak.

Y-Type zeolites showed broad unresolved spectra. Imperfection of the resolution indicates the overlap of various components desorbing at a relatively broad temperature range. Such a complexity in the TPD spectra of NH_3 taken from faujasite-type zeolites has already been reported by Cattanach *et al.* (10). HY had a long tailing up to 700 K which was not observed on NaHY. The preferential elimination of strong acid sites by cation exchange has

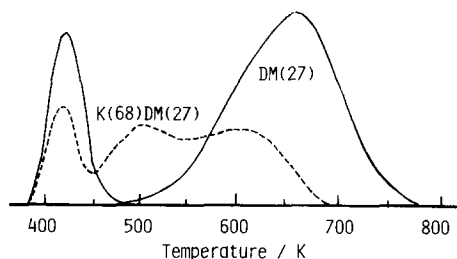


FIG. 4. TPD spectrum of NH_3 from K(63)DM(27) with that from DM(27).

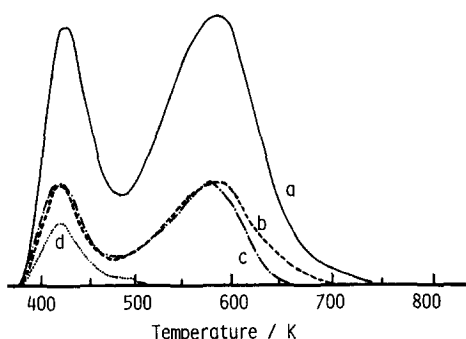


FIG. 5. TPD spectra of NH_3 from ZSM-5: (a) HZSM-5(38); (b) HZSM-5(56); (c) HZSM-5(103); (d) K(63)HZSM-5(56).

thus been confirmed as on mordenite and ZSM-5. Amount of desorbed NH_3 and T_M on these zeolites are summarized in Table 1, including results on CaHM and RbHY.

Heat of adsorption of ammonia (ΔH) is evaluated in the TPD experiment by the usual equation first described by Cvetanovic and Amenomiya (17),

$$2 \ln T_M - \ln \beta = \Delta H/RT_M + C$$

where β and C denote the rate of temperature increase and a constant relevant to the experimental condition, and T_M and R are maximum temperature and gas constant, respectively. The shift of maximum temperature was measured as a function of β , and ΔH was measured from the plots in Fig. 7; 67 and 145 kJ/mol were obtained on HM for l and h peaks, respectively.

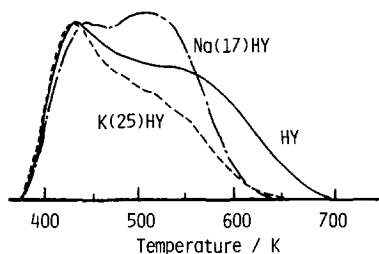


FIG. 6. TPD spectra of NH_3 from Y-zeolites.

Infrared Spectroscopy of Hydroxide and Ammonia Adsorbed

As it has been already reported (16), HM gave ir absorptions of OH at 3740 and 3600 cm^{-1} which were usually identified as Si—OH and Brønsted acidic hydroxide, respectively (18). Adsorption of ammonia diminished completely the latter hydroxide band only and gave rise to the appearance of NH_4^+ band at 1447 cm^{-1} . The band of NH_3 adsorbed on Lewis acid sites was hardly observable, although the adsorption of pyridine yielded the species thereon (16). Subsequent evacuation of this material at 373 and 573 K restored the 3600- cm^{-1} band with a gradual decrease of the ammonium band. Evacuation at 673 K completely desorbed NH_3 in agreement with the TPD experiment.

The method mentioned here was applied to K- or Ca-HM, DM and ZSM-5 to compare their acidity profiles. However, no difference less than a subtle shift of OH band

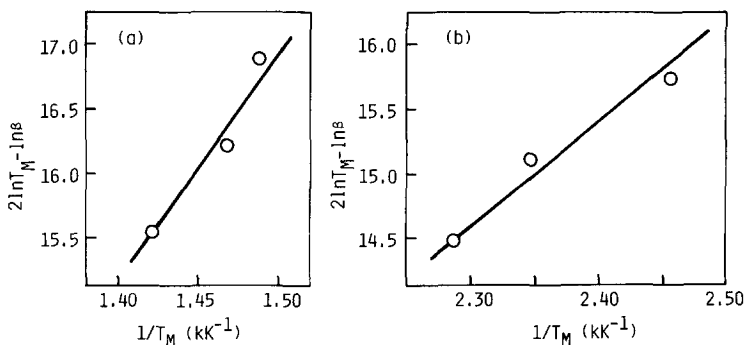


FIG. 7. Plots of $(2 \ln T_M - \ln \beta)$ against $1/T_M$ for the h (a) and l (b) peaks on HM.

could be observed upon adsorption of NH_3 and further successive evacuation.

Intensity of OH band at 3600 cm^{-1} and of NH_4^+ band at 1447 cm^{-1} was then measured quantitatively to correlate with the amount of desorbed ammonia in the TPD experiment.

As mentioned above, a decrease in NH_4^+ band upon evacuation was always followed by an increase in the OH band at 3600 cm^{-1} . This correspondence between ammonia adsorbed and hydroxide was observed quantitatively, as shown in Fig. 8. The amount of NH_3 desorbed as *l* and *h* peaks and their total amount were respectively correlated with the relative concentration of OH observed at 3600 cm^{-1} . Furthermore, the total amount of desorbed NH_3 was plotted against the intensity of ammonium band at 1447 cm^{-1} evacuated at 373 K , and a good correlation was obtained as shown in Fig.

9. The ir intensity of NH_4^+ band which was measured upon evacuation at 573 K was also correlated with the amount of NH_3 desorbed at temperatures higher than 573 K . These correlations between ir spectroscopy and TPD indicate that ammonia is chemisorbed on Brønsted acid sites and the two desorption peaks of NH_3 in the TPD spectra reflect the amount and strength of the acidity.

DISCUSSION

TPD spectra of NH_3 have already been reported on mordenite (7), Y-faujasite (10), and ZSM-5 type (5, 6, 8, 9) and discussed on the basis of comparisons with ir (6, 7) and benzene interaction (7). Ammonia is an excellent probe molecule of TPD for the measurement of acid property of zeolite, because it can be stabilized on acid sites and can penetrate into pores due to its strong basicity and small size. However, the transport of this base molecule into the zeolite material may not be completely rapid. In some cases, the thermal behavior could be influenced by these diffusion problems. Such condition may be plausible at lower temperatures, since Kanazirev (11) used TPD of NH_3 for studying the problem of diffusion in the nonacidic zeolite matrix. Very broad peak of TPD of NH_3 observed in previous studies at temperatures around or lower than 373 K may be influenced by the diffusibility of ammonia. The present investigation used a relatively high temperature (373 K) for attaining equilibrium with the zeolite surface to eliminate the broadness of the TPD spectra. Furthermore, the rate of temperature increase was slow compared with those of previous ones, which made the spectrum well resolved.

Not only the amount of acid site but also the distribution of acid strength can be surmised from the TPD spectra. The value of heat of adsorption obtained in the present method (145 kJ/mol) is approximately in agreement with that obtained from microcalorimetry, $135\text{--}145\text{ kJ/mol}$ (3, 4) and ca. 170 kJ/mol (19). From this point of view,

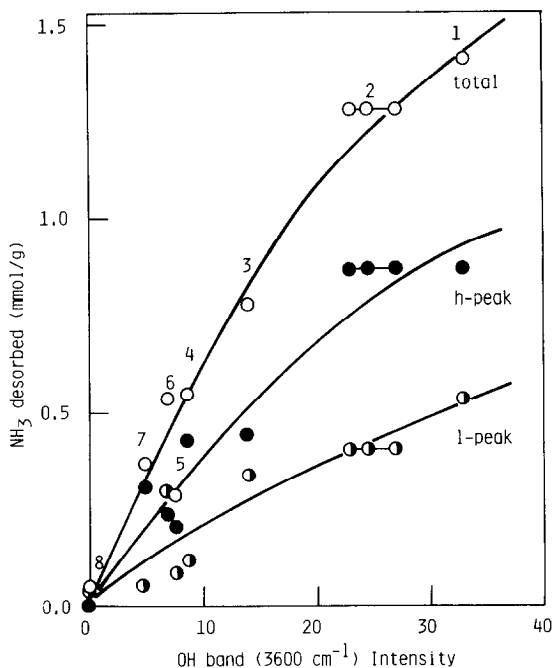


FIG. 8. Relationship of the amount of ammonia desorbed in *l*- and *h*-peaks and their total amount with the ir intensity of hydroxide band at 3600 cm^{-1} : (1) Ca(24)HM; (2) HM; (3) K(37)HM; (4) DM(27); (5) HZSM-5(56); (6) K(53)HM; (7) DM(71); (8) K(63)HZSM-5(56).

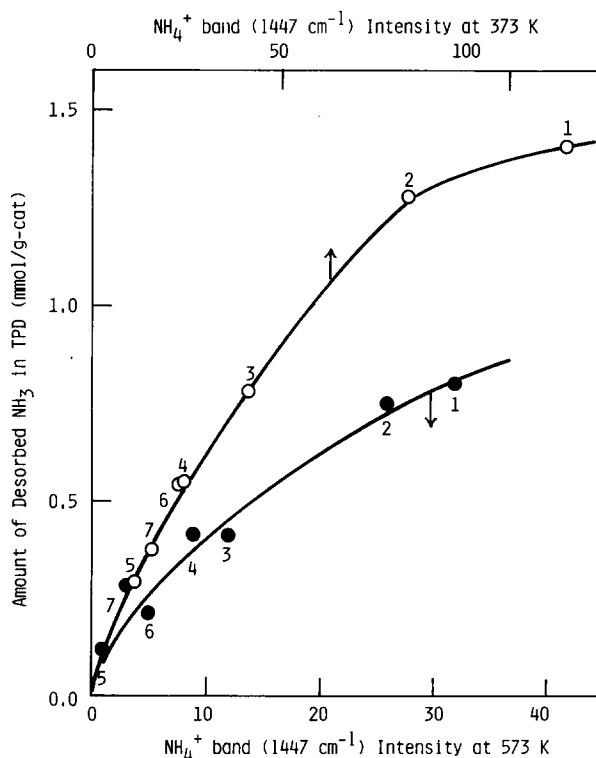


FIG. 9. Relationship between amount of desorbed NH_3 in TPD and ir intensity of NH_4^+ band at 1447 cm^{-1} . The ir intensity observed upon evacuation at 373 and 573 K are plotted against the amounts of NH_3 desorbed above 373 and 573 K, respectively.

zeolites used in this study are reported to have the following order according to their acidity strength, i.e., mordenite $>$ ZSM-5 $>$ Y-faujasite. This order of acidity strength agrees with that derived from calorimetry (3, 19).

Some data concerning the acid amount have been reported where microcalorimetry (3) as well as traditional titration methods (20–22) were employed. In Table 1, obtained acid amounts are compared with those reported values. One can thus confirm the agreement between them on HM and NaHY (SK-41).

One of the interesting remarks of the TPD spectra is the appearance of two peaks particularly on HM and HZSM-5. Identification of these peaks has already been described using the ir spectroscopy on mordenite (7) and ZSM-5 (6). The peak desorbed at higher temperature (*h*-peak)

was always assigned to ammonia adsorbed on the acidic hydroxide at 3600 cm^{-1} . The suspect is valid also in the present study, because the amount of *h*-peak was well correlated with the concentration of OH at 3600 cm^{-1} . On the other hand, the *l*-peak was not completely analyzed, and the identification seems to be still a matter of controversy. The peak observed at ca. 500 K, i.e., what Topsøe *et al.* called the β -peak, was identified as Si—OH at 3740 cm^{-1} or nonzeolitic impurity (6). Mirodatos *et al.* indicated some possibility about the origin of the peak on H-mordenite (7). Other than the Si—OH band at 3720 – 3740 cm^{-1} and protonic sites not related to hydroxyls, the broad band from 3350 to 3650 cm^{-1} was assumed to be the site corresponding to *l*-peak. However, the amount of *l*-peak as well as that of *h*-peak correlates well with the intensity of the 3600-cm^{-1} band (Fig. 8).

This suggests that the *l*-peak also has some relevance to the ir intensity observed at 3600 cm^{-1} . Therefore, it is most likely that the *l*-peak is attributed to ammonia adsorbed on OH observed as broad bands at 3350 to 3650 cm^{-1} . However, the specificity of zeolite species may have to be considered, and much work will be needed in order to fully understand this problem.

As stated above, TPD of ammonia can be considered to be an effective method in characterizing the acid property of zeolites. Relative rapidness of the experiment and sufficient precision add an advantage to this method.

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