# Temperature-Programmed Desorption of Ammonia on Zeolites. Influence of the Experimental Conditions on the Acidity Measurement

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(Received April 17, 1986)

The Influence of the experimental conditions of the TPD (Temperature-Programmed Desorption) of ammonia on the measurement of acidity of mordenites and Y zeolites was studied. The results were applicable to the measurements of the strength and the number of acid sites of zeolites. For contact times of the carrier gas from $10^{-2}$ to $10^{-6}$ g min ml$^{-1}$ defined as $W/F$ ($W$, sample weight; F, flow rate of the carrier gas), the peak maximum temperature was related to the parameter ($W/F$). The relationship was explained on the basis of a theoretical equation derived by Cvetanović and Amenomiya under the conditions of readsorption. Ammonia is readsorbed on zeolites under these conditions, and one has to use the experimental conditions of the same contact time in order to evaluate the acid strength of zeolite from the peak maximum temperature. On the other hand, the ratio of intensity of low temperature peak (l-peak) to that of the high temperature peak (h-peak) increased with increasing the contact time of the carrier gas. This relation suggested that the l-peak intensity depended upon the degree of evacuation of the weakly-held ammonia. The l-peak is ascribable to very weakly or physically adsorbed ammonia on zeolites, and only the h-peak has to be accounted for to measure the number of acid sites.

Currently, much attention is focused on the activity and selectivity of catalytic reactions over acid-type zeolites. Because the acidity as well as the structure strongly affects the catalytic activity, it is of extreme importance to characterize the zeolite catalyst from the viewpoint of the acidity. Usually, the acidity of zeolite can not be measured by the titration method using Hammett indicators, because the diffusion of base molecules may be strictly retarded due to the small pores of the zeolite. Temperature-programmed desorption (TPD) of ammonia[1-3] and the microcalorimetry of differential heat of adsorption of ammonia[4] have been recommended.

One of the authors has already reported the usefulness of TPD of ammonia for the measurement of the acidity, and has compared the strength and number of acid sites of various zeolites.[1] This method is preferable to others because of the rapidness of the experiment. However, some problems remain unsolved. Firstly, the experimental conditions including sample weight, flow rate of carrier gas, rate of increasing temperature, partial pressure within the cell, etc., have to be examined in more detail to determine the acidity precisely. Although some criteria were proposed theoretically to design the conditions,[5] no experimental confirmations were attempted. Secondly, the identification of desorption peaks is still a matter of controversy: the origin of the l-peak (desorbed at ca. 323 K) is not clearly known, although the h-peak (another peak desorbed at a higher temperature) is attributed to an IR absorption band at 3600 cm$^{-1}$.[1,2]

We started a project on the TPD of ammonia under the organization of the Catalysis Society of Japan, committee of reference catalysts. Five kinds of acid-type mordenite and Y zeolites were distributed to research groups in universities and industrial companies. Each group measured the acidity of zeolites using TPD of ammonia by their own procedures, some of the conditions being unified. Results thus obtained were compared and discussed. As a result of the cooperative work, important conclusions were obtained about the acidity measurement using the TPD of ammonia. In this communication, we will report on the influence of experimental conditions on the measurement of acidic strength and amount of zeolites.

## Experimental

Zeolites Reference Catalysts (JRC-Z) were supplied by the Catalysis Society of Japan: Some properties are shown in Table 1. All of them had been converted into the decationized form before distribution, and no pretreatment except for the evacuation was performed before the measurements.

Only the following experimental conditions were unified:

(1) pretreatment: evacuation at 773 K for 1 h.
(2) adsorption of ammonia, at 373 K.
(3) increase of bed temperature, at a rate of 10 K min$^{-1}$ from 373 K.

Other experimental conditions were chosen individually, as shown in Table 2. Experimental methods were divided into those of vacuum and of flow. Intensity of desorbed ammonia was detected by thermal conductivity detector (tcd), mass spectroscopy (ms), gravimetry, or vacuum gauge. The carrier gas, helium, was made to flow into the zeolite bed with or without pumping, or the zeolite was pumped to evacuate the desorbed ammonia.

The strength and amount of acidic sites were measured by the peak maximum temperature and the desorbed amount.

## Results and Discussion

**Dependence of Desorption Temperature on Experimental Conditions.** The TPD spectra obtained were characteristic of two desorption peaks (l- and h-peaks at low and high temperatures, respectively) on not only mordenite but also Y-zeolite (Fig. 1), which was in agreement with in the previous study.[1] The resolu-

Table 1. List of Zeolites Used in This Study[a)]

| Name | Structure | ($SiO_2/Al_2O_3$) ratio | (%) of $H^+$ exch. | Surf. Area ($m^2 g^{-1}$) Total | Ext.[b)] | Crystal Habit |
|---|---|---|---|---|---|---|
| JRC-Z-HM10 | Mordenite | 9.9 | 98 | 187 | 9.8 | Rod |
| JRC-Z-HM15 | Mordenite | 14.9 | 99 | 309 | 13.5 | |
| JRC-Z-HM20 | Mordenite | 19.9 | 99 | 299 | 15.2 | Cube |
| JRC-Z-HY4.8 | Y | 5.2 | 99 | 646 | 17.0 | |
| JRC-Z-HY5.6 | Y | 5.6 | 72 | 634 | 10.6 | |

a) Prepared by ion exchange with corresponding Na-form zeolites in a $NH_4Cl$ solution, followed by calcination at 673 K for 2 h. b) Measured by the benzene-filled pore method, see Ref. 6.

Table 2. List of Measurement Conditions

| No. | Method | Detector | Samp. Wt. (W) (g) | Flow Rate/$f$[a)] (ml(STP) min$^{-1}$) | Cell Press. ($p$)[b)] (Torr) | $W/F$[c)] g min ml$^{-1}$ |
|---|---|---|---|---|---|---|
| 1 | Vacuum | gauge | 0.15 | Unknown | Unknown | — |
| 2 | Flow | gravimetry | 0.1 | 100 | Ambient | $1.0\times10^{-3}$ |
| 3 | Flow | ms | 0.005 | 40 | 380 | $6.3\times10^{-5}$ |
| 4 | Flow | tcd | 0.5 | 30 | Ambient | $1.7\times10^{-2}$ |
| 5 | Flow | tcd | 0.1 | 30 | 50 | $2.2\times10^{-4}$ |
| 6 | Flow | ms | 0.05 | 50 | Ambient | $1.0\times10^{-3}$ |
| 7 | Flow | ms | 0.0018 | 10 | 495 | $1.2\times10^{-4}$ |
| 8 | Flow | tcd | 0.5 | 80 | 360 | $3.0\times10^{-3}$ |
| 9 | Flow | tcd | 0.2 | 60 | 30 | $1.3\times10^{-4}$ |
| 10 | Flow | tcd | 0.01—0.5 | 20—60 | 35 | $7.6\times10^{-6}$—$9.2\times10^{-4}$ |

a) Measured in ambient pressure. b) The pressure in the TPD cell was below the ambient pressure when the carrier gas was pumped. c) $F=760\ f/p$. d) 1 Torr=133.3 Pa.

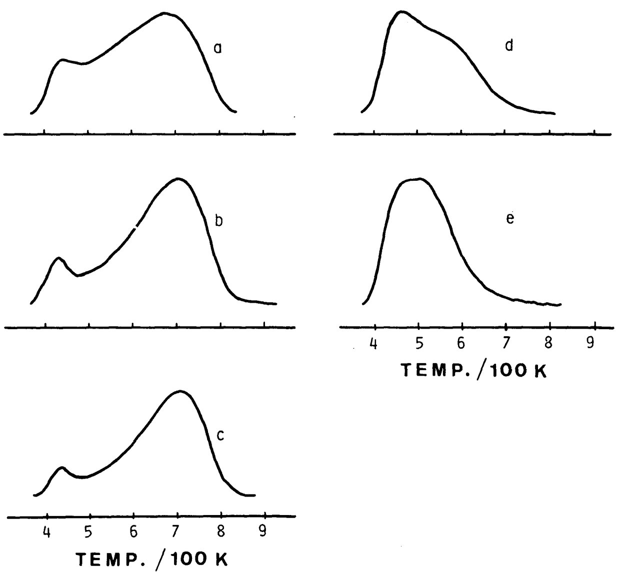

Fig. 1. Typical example of TPD spectra on Zeolites HM-10 (a), HM-15 (b), HM-20 (c), HY-4.8 (d), and HY-5.6 (e) obtained in the $W/F$ of $7.7\times10^{-5}$ g min ml$^{-1}$. Spectrum intensity was shown in an arbitrary units divided by grams of zeolite. Temperatures for the h-peak maximum were 680 (a), 703 (b), 705 (c), ca. 590 (d), and ca. 490 K (e).

tion of double peaks was good in cases of mordenites, but imperfect in those of Y-zeolites. The acid strength of these zeolites could be summarized due to the comparison between peak maximum temperatures of the h-peak. The comparison consistently afforded the following sequence for the acidity strength:

**HM-15≥HM-20>HM-10≫HY-4.8>HY-5.6**

However, the desorption temperatures did not agree at all, when comparisons were made between those obtained by various groups. For example, the peak temperature on the HM-15 was distributed from 673 to 883 K. In order to understand such a large difference, we examined experimental conditions relevant to the desorption temperature. Although various experimental methods were included in these experiments, such a large difference could not be understood only by differences in apparatus or in measuring the temperature.[7)] It was thus found that the desorption temperature was correlated with the contact time of the carrier gas $W/F$, where $W$ and F denoted the zeolite weight and the flow rate of carrier gas. If the carrier gas was pumped, F should be replaced by a corrected flow rate 760 $f/p$, where $p$ was the pressure in the TPD cell in Torr (1 Torr=133.3 Pa), and $f$ was the flow rate measured in atmospheric pressure, because the carrier gas was made to flow at a faster rate than under atmospheric conditions. The relationship in the case of the HM-15 is shown in Fig. 2; the peak temperature gradually increased with increasing the contact time $W/F$ in the range of $10^{-2}$ to $10^{-6}$ g min ml$^{-1}$.

According to the kinetical analysis of the TPD spec-

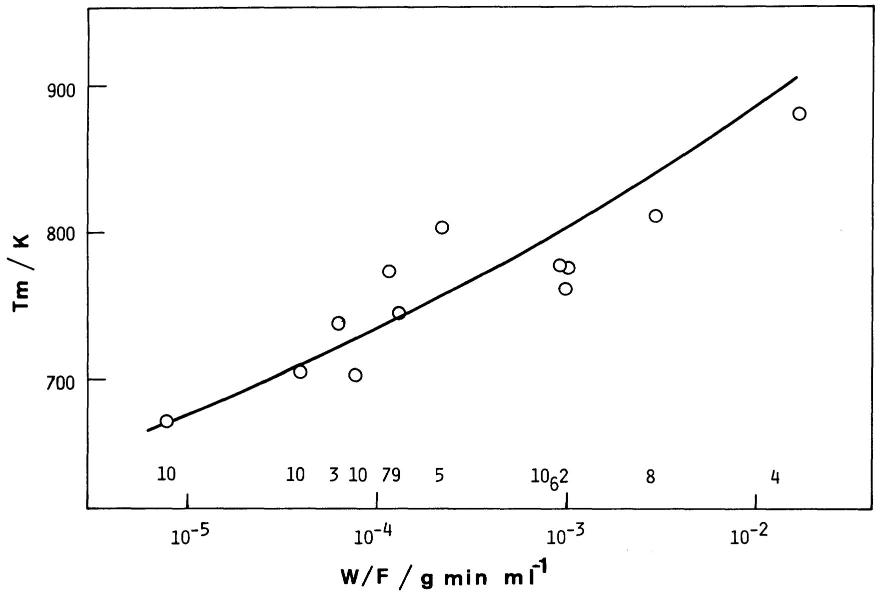

Fig. 2. Correlation between the peak maximum temperature and the *W*/F on HM-15. The theoretical curve was simulated for the parameters. $\beta$: 10 ($\mathrm{K\,min^{-1}}$), $\Delta H$: $1.5\times10^5$ ($\mathrm{J\,mol^{-1}}$), $\theta$: 0.35, $\rho$: 0.5, *R*: 8.31 ($\mathrm{J\,K^{-1}\,mol^{-1}}$). Experimental run numbers in this Figure are referred to in Table 2.

tra by Cvetanović and Amenomiya,[8] the conditions of the TPD experiment are divided into three limiting cases: (a) When the readsorption of a desorbed molecule does not occur, (b) when the readsorption occurs freely, and (c) when the diffusion controls the desorption. The correlation found in this study indicates that the present experiments are carried out under the readsorption conditions, because, in case (b), the peak maximum temperature (Tm) is theoretically correlated with the contact time:

$$2\log T_\mathrm{m} - \log\beta = \Delta H/2.303RT_\mathrm{m} + \log Q$$
$$Q = (1-\theta)^2 V\Delta H/FAR$$
$$V = W/\rho$$

Here $\beta$ and $\theta$ show the rate of temperature increase and the coverage at peak maximum, $\Delta H$ and *R* are heat of adsorption and gas constant, and *V* and $\rho$ are the volume and density of solid. Parameter *A* is equal to $\exp(\Delta S/R)$, where $\Delta S$ is the increase of entropy upon desorption. After the values of parameters were assumed, theoretical relations could be calculated, as shown in Fig. 2. When *A* is assumed to be $2.86\times10^5$, the simulated curve follows the relation between the peak temperature and *W*/F. One can thus conclude that ammonia was freely readsorbed on these zeolites in the TPD experiment, and the peak temperature depends on the contact time of the carrier gas.

The conclusion is in agreement with the theoretical consideration by Gorte[5]: He showed that the desorption temperature was changed by several hundreds K due to the effect of the readsorption on the porous catalyst. Additionally, Demmin and Gorte[5] reported on the influence of the crystal size on the desorption temperature. According to their analysis, a temperature gradient exists along the catalyst bed, when the $Fr^2\rho/3WD$ is larger than 0.1, where *r* is the radius of the crystal and *D* is the diffusion constant. In such a case, the desorption temperature will be affected by the diffusion of molecules inside the pore, and the peak maximum temperature will not correspond to the strength of the acid sites. When these parameters are assumed: $r$=1 μm; $D=10^{-5}\ \mathrm{cm^2\,s^{-1}}$, their proposed conditions are satisfied only in less than $2.7\times10^{-5}$ g min $\mathrm{ml^{-1}}$ of *W*/F, and almost all the present experiments are carried out under different conditions. Furthermore, it was found experimentally that the sequence of zeolites in order of the acid strength did not change throughout these experiments. Therefore, the influence of crystal size on the judgment of the acid strength may be disregarded, as far as the present experiments are concerned. Measurements on larger crystals seems to be required for the confirmation of the influence of crystal size.

This method has recently been used frequently by many researchers. However, these measurements are utilized only for a relative comparison of the acidities of their own zeolites, but not for comparisons with findings reported elsewhere. However, the present conclusion indicates the possibility of comparison of the strength of zeolite acidities which were obtained by TPD of ammonia, if only some parameters such as *A* and $\Delta H$ are given. Therefore, from now on, the experimental conditions of contact time of carrier gas must be described together with the experimental results.

**Identification of Low Temperature Peak.** Desorbed amounts of ammonia measured by various groups distributed significantly. For example, the desorbed amounts from HM-15 were 1.09—3.18 and 0.21—1.87

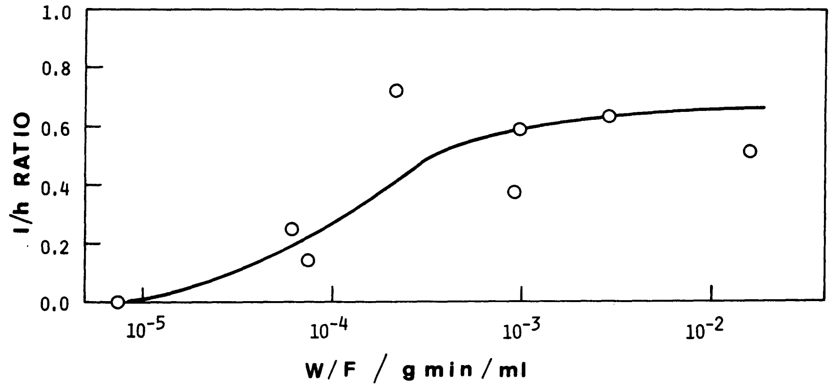

Fig. 3. Correlation between the peak intensity ratio (l-/h-peaks) and the *W*/F.

(mmol g$^{-1}$) in the h- and l-peaks, respectively. The distribution in the h-peak was not, however, related with any experimental conditions or measurement method. Experimental errors were probably included in measuring the desorbed amount. On the other hand, the intensity ratio of the l- to h-peaks which was used in order to compensate for the experimental errors in the quantitative measurements was related with the contact time *W*/F, as shown in Fig. 3. The intensity of l-peak was almost negligible at the small contact time, and the intensity relative to that of h-peak increased with increasing the contact time. This trend indicates that the l-peak does not depend on the catalyst property, but on the experimental conditions.

Furthermore, it was found that the Na-mordenite possessed only the l-peak, whose amount was much greater than that on the decationized one (Fig. 4). The appearance of the desorption spectrum at this temperature has been already reported on non-acidic zeolite by Kanazirev,[9] who measured the TPD for the study of diffusion processes.

These findings indicate that the l-peak of the mordenite does not originate from molecules adsorbed on the weak-acid site but from physically or very weakly chemisorbed molecules. The dependence of the l- to h-peak ratio on the contact time may be caused by the degree of the removal of the weakly-held ammonia. Under the conditions of the large contact time, i.e. slow flow rate of the carrier gas and/or large amount of zeolites, the weakly-held ammonia is difficult to remove by evacuation, and some molecules remain undesorbed. Those remaining molecules may be desorbed as the l-peak upon increase of the bed temperature. In other words, the l-peak could be regarded as the *remainder* of the desorbable ammonia. Therefore, it is concluded that only the h-peak has to be accounted for to measure the acidity of zeolites.

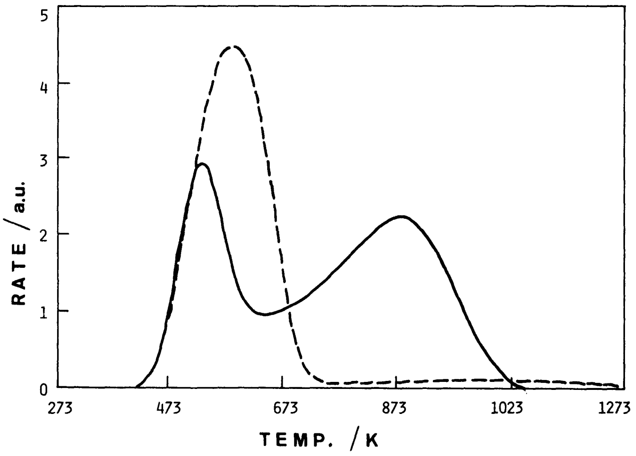

Fig. 4. Comparison between spectra on HM-15 (solid line) and on M-15 (Na-mordenite)(dotted line). These were obtained in the *W*/F of $1.7\times10^{-2}$ (g min ml$^{-1}$).

The method of removal of gaseous ammonia was not strictly determined. However, it is practical to require that the removal of gaseous ammonia should be done until the detector reaches the base level. In these conditions, small amounts of desorbed ammonia may be undetectable, and a desorption peak will be readily found as the l-peak. The completely evacuation of ammonia is difficult and impractical, because it requires a long time, and the extent of evacuation is not properly decided.

On the other hand, the NaY-zeolite showed only a smaller intensity of the l-peak than the HY, unlike the mordenite. For example, in the experiment of run number 1 (see Table 2), the amount of ammonia desorbed from Y-4.8 (NaY type) was 0.08 (mmol g$^{-1}$), while that from HY-4.8 was 1.87 (mmol g$^{-1}$). Although it is difficult to analyze precisely the components of the TPD spectra on the HY-zeolite because of the poor resolution, the peak appearing in the low temperature seems to be easily evacuated due to the large pore size of the Y-zeolites.

Prof. Yasuhiko Kurusu of Sophia Univ., Prof. Yuan Nai-Ju of Qinghua Univ., Mr. Makoto Nakamura, Mr. Yoshimasa Inoue, Dr. Yukuaki Mitarai, and Dr. Yasuo Takami of Sumitomo Metal Mining, Mr. Tetsuya Imai, and Mr. Kozo Iida of Mitsubishi Heavy Ind., Mr. Masahiro Tajima, and Prof. Shuichi Kagawa of

Nagasaki Univ., Mr. Sotaro Nakamura, Mr. Masao Ishii, and Mr. Kiyonari Matsuoka of Shindaikyowa Petrochemical Ind., Mr. Hiroshi Sato, Mr. Ken-ichi Hirose, and Mr. Hiroshi Ichihashi of Sumitomo Chemical, Mr. Masaru Ushio, and Mr. Takeshi Ishii of Nippon Oil, Mr. Takahiro Kawamura, Mr. Shigeo Baba, and Mr. Toshio Shimizu of Cosmo Oil, Prof. Yuukei Takasaki, and Mr. Takemi Shibuya of Utsunomiya Univ., and Mr. Masahiko Sawa of Nagoya Univ. are thanked for supplying experimental data and helpful discussions.

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7) a) Design of the TPD cell, for example, the size of cell diameter or the preheating of the carrier gas could affect the measurement of temperature; b) Metal pipes and connectors should be avoided, if possible, since ammonia could interact with the metal.

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