CHEMISTRY LETTERS, pp. 1147-1148, 1981.

MEASUREMENT OF THE ACID AMOUNT AND STRENGTH OF MORDENITES BY THE TEMPERATURE-PROGRAMMED DESORPTION OF AMMONIA

Hirofumi ITOH, Tadashi HATTORI, and Yuichi MURAKAMI
Department of Synthetic Chemistry, Faculty of Engineering,
Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464

Temperature-programmed desorption of ammonia on mordenites has been examined. The amount and strength of acid sites of mordenites can be quantitatively determined by the TPD method. The strong acid sites of H-mordenite are selectively ion-exchanged with potassium ions.

Zeolite is a well-known acid catalyst and its acid properties have been extensively investigated[1,2]. The acid properties are mainly characterized by the Hammett titration method and IR spectra of adsorbed pyridine. These methods, however, cannot be applied to small pore zeolites such as mordenite and ZSM-5[3,4]. These zeolites have attracted wide attention because of their shape selectivity. Acid properties of these zeolites have been examined by the microcalorimetric measurement of the differential heat of adsorption of ammonia[4,5]. Forni has suggested the possibility of determining acid strength by the temperature-programmed desorption (TPD) spectra[6]. The acid nature of ZSM-5 has been qualitatively examined by the TPD spectra of NH_3[7].

H-mordenite (HM) is commercially supplied by Norton Company (Zeolon 100). KHM(29) and KHM(41) were prepared by the conventional ion-exchange of HM with an aqueous solution of potassium acetate. The numerals in parentheses show the degree of ion-exchange. TPD spectra were measured with a conventional TPD apparatus[8]. About 0.5 g sample in a TPD cell was evacuated at 773 K for 1.5 h, exposed to ammonia 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 K with a heating rate of 2.5 $K \cdot min^{-1}$ and with helium as carrier gas having a flow rate of 60 $cm^3 \cdot min^{-1}$.

Figure 1 shows that the TPD spectra of ammonia on mordenites had two peaks named *l* and *h* peaks. The amount of desorbed ammonia of *l* and *h* peaks on HM were 0.41 and 0.87 $mmol \cdot g^{-1}$, respectively. Auroux *et al.* have reported that the amount of strong acid sites of HM determined by microcalorimetry is 0.73 $mmol \cdot g^{-1}$ and that of total acid sites is 1.24 $mmol \cdot g^{-1}$ from the chemical formula[5]. The total amount of desorbed ammonia (*l* + *h*) in the present study was 1.28 $mmol \cdot g^{-1}$ in good accordance with the above-mentioned value. The amount of desorbed ammonia of *h* peak also is in good accordance with the amount of strong acid sites. These facts indicate that the amount of total and strong acid sites can be determined by the TPD spectra of ammonia.

The strength of acid sites can also be quantitatively measured by the TPD method. When the readsorption of desorbed molecules is in equilibrium, the heat of adsorption (ΔH) is related to the temperature at the peak maximum (T_M) and to the heating rate (β)[8]. Figure 2 shows a plot of $2 \ln T_M - \ln \beta$ against $1/T_M$ on HM. The heat of adsorp-

tion calculated from the slope of the plot was 145 kJ/mol, which is in good agreement with the differential heat of adsorption of 145-125 kJ/mol determined by microcalorimetry. Since the differential heat of adsorption of NH_3 is considered to represent the strength of acid sites, this agreement indicates that the acid strength can be measured by the TPD method, and that the T_M value obtained under the same condition can be a measure of the acid strength.

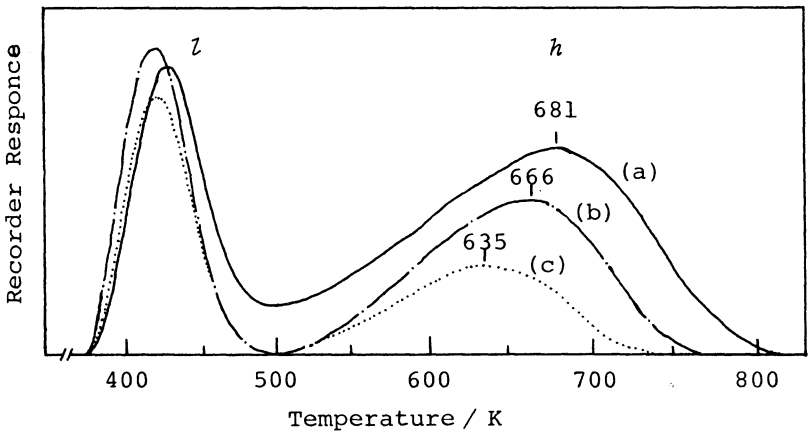

Fig. 1. TPD spectra on HM (a), KHM(29) (b) and KHM(41) (c). Heating rate, 2.5 K·min^{-1}; sample weight, ca.0.5g.

As can be seen from Fig. 1, the ion-exchange of HM with potassium ion reduced both the amount and strength of *h* peak with *l* peak remaining essentially unchanged. These results indicate that the strong acid sites are selectively ion-exchanged resulting in the decrease in the amount and strength of strong acid sites. This tendency agrees with the change in the acid distribution of a series of H-Na-Y[9].

In summary, the amount and strength of acid sites can be quantitatively determined by the TPD method.

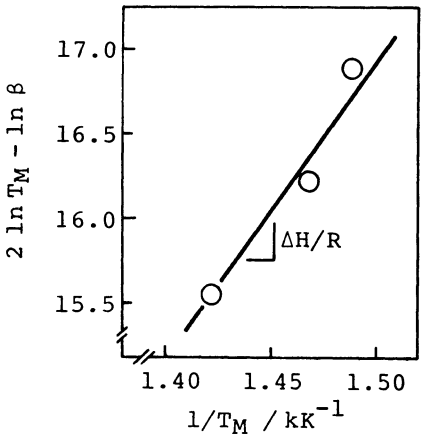

Fig. 2. Plot of (2 ln T_M - ln β) against 1/T_M on HM.

References

1) H.A. Benesi and B.H.C. Winquist, Adv. Catal., 27, 97 (1978).
2) D. Barthomeuf, Proc. 4th Int. Conf. Molecular Sieves, 453 (1977).
3) W.F. Kladnig, J. Phys. Chem., 83, 765 (1979); D. Barthomeuf, ibid., 83, 766 (1979).
4) J.C. Vedrine, A. Auroux, U. Bolis, P. Dejaifve, C. Naccache, P. Wierzchowski, E.G. Derouane, J.B. Nagy, J-P. Gilson, J.H.C. van Hooff, J.P. van den Berg and J. Wolthuizen, J. Catal., 59, 248 (1979).
5) A. Auroux, V. Bolis, P. Wierchowski, P.C. Gravelle and J.C. Vedrine, J. C. S. Faraday Trans. I, 75, 2544 (1979).
6) L. Forni, Catal. Rev., 8, 65 (1973).
7) J.R. Anderson, K. Foger, T. Mole, R.A. Rajadhyaksha and J.V. Sanders, J. Catal., 58, 114 (1979); T. Yashima, Y. Sakaguchi and S. Namba, Proc. 7th Int. Cong. Catalysis, Tokyo, Part A, 739 (1980).
8) R.J. Cvetanović and Y. Amenomiya, Adv. Catal., 17, 103 (1967).
9) S. Namba, T. Yashima, Y. Itaba and N. Hara, "Catalysis by Zeolites", p105 Elsevier Scientific Publ. Co., Amsterdam, (1980).

(Received June 26, 1981)