B-AD-026

Ammonia Temperature Programmed Desorption (NH_3-TPD) Measurement -Investigation of Desorption Energy and Heat of Adsorption-

Introduction

Acid zeolite's catalytic activity is greatly affected by the acidic points on its surface. Knowing the strength and quantity of these acidic spots is essential for the evaluation of acid zeolites. Calorimetry and ammonia TPD have been used to determine these properties. However, since calorimetry requires skill and it is difficult to determine the pretreatment temperature of catalyst samples, it is now possible to easily determine the acid strength, acid amount, and heat of adsorption by using commercially available automatic temperature programmed desorption equipment (BELCATII).

Temperature Programmed Desorption (TPD) was first proposed by Amemiya and Cvetanovic in 1963.[1)] In TPD, an adsorbent is adsorbed at equilibrium under predetermined conditions, and then the temperature is raised to a constant level. The molecules are desorbed when the thermal energy exceeds the adsorption energy of the pre-adsorbed molecules. The molecules desorbed from the surface are carried by the carrier gas and quantified by the detector. Detectors such as thermal conductivity detectors (TCD) and mass spectrometers (MS) are used for this purpose. Amemiya et al. found that if the adsorption on the surface is uniform and re-adsorption and diffusion are negligible, the temperature rise rate and activation energy can be expressed as the following equation.[2)]

$$log\left(\frac{T_P^2}{\beta}\right) = \frac{E_d}{2.303RT_P} + log\left(\frac{E_d A_0}{RC}\right) \quad (1)$$

Tp	Peak desorption temperature (K)
β	Temperature rise rate (K/min.)
Ed	Desorption energy (kJ/mol)
A0	Amount of adsorption
C	constant (related to desorption rate)

The peak desorption temperature shifts when the temperature rise rate is changed. If log(Tp2/β) is plotted to 1/Tp, a linear relationship is obtained, and the desorption energy (Ed) can be obtained from the slope. In the case of free re-adsorption, the heat of adsorption (ΔH) can be obtained from the same plot[2)]. Murakami and Niwa proposed the following equation based on the insufficient equation of Amemiya et al.

$$ln(T_P) - ln\left(\frac{A_0 W}{F}\right) = \frac{\Delta H}{RT_P} + ln\left(\frac{\beta(1-\theta)^2(\Delta H - RT_P)^2}{P^0\, exp(\Delta S / R)}\right) \quad (2)$$

W	Sample weight (g)
F	Actual flow rate (ml/min.)

θ coverage at peak temperature

P0 : Normal pressure

This equation shows that the peak temperature is affected not only by the contact time but also by the amount of acid. ln(Tp)-ln(A0W/F) plotted against 1/Tp gives a linear relationship and the slope can be used to determine the heat of adsorption (ΔH).

Experiment

1. In the TPD measurement, the desorption energy (Ed) of JRC-Z5-25H is determined by the Amemiya equation by changing the temperature rise rate.

Equipment : BELCATII
Sample : JRC-Z5-25H(MFI)
Sample weight : 0.04949 g (using the same sample for all measurements)
Carrier gas flow rate : He 30sccm

pretreatment program

Gas used	min	Target temperature
0:He	50	500
0:He	60	500
0:He	40	100
0:He	10	100
4: NH3	30	100
0:He	5	100

Measurement program

TCD stability latency	20 min
Target temperature	500 °C
Temperature rise rate	2, 5, 10, 15 °C/min
Target temperature holding time	30 min

2. Calculate the heat of adsorption (*ΔH*) of JRC-Z5-25H by changing the sample weight in the TPD measurement using the Murakami-Tanba equation.

Equipment : BELCATII
Sample : JRC-Z5-25H (MFI)
Sample weight : 0.03522g,0.03761g,0.04293g,0.06825 g (using each weigh for each measure)
Carrier gas flow rate : He 30sccm

pretreatment program

Gas used	min	Target temperature
0:He	50	500
0:He	60	500
0:He	40	100
0:He	10	100
4: NH3	30	100
0:He	5	100

Measurement program

TCD stability latency	20 min
Target temperature	600 °C
Temperature rise rate	10 °C/min
Target temperature holding time	30 min

Result

1. Results of desorption energy calculation using the Amemiya equation

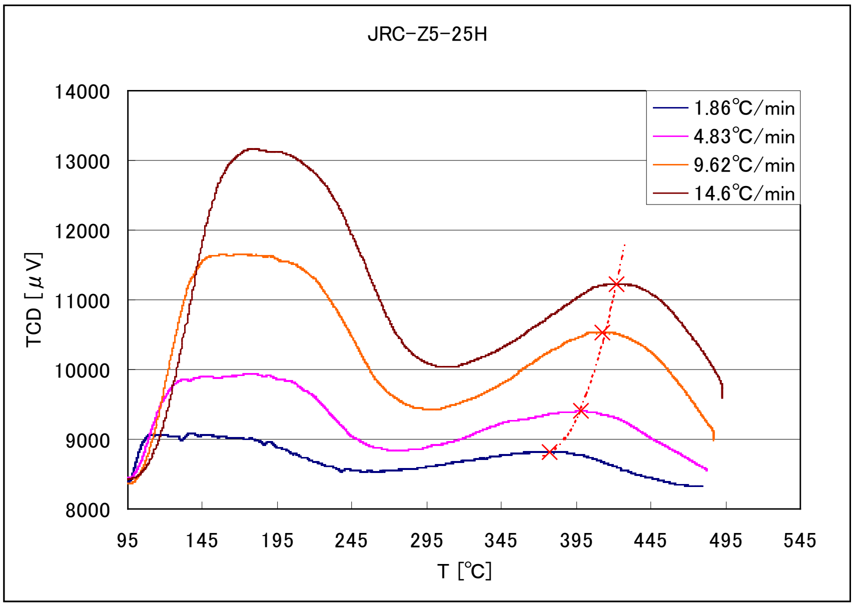

Figure 1. TPD curve for JRC-Z5-25H by changing temperature rize rate

Table 1 Numerical data by TPD

Temperature rise rate (°C/min)	Sample weight	file-name	Peak temperature	Log(Tp2/β)	1/Tp	log(W/F)+3
2.00	0.04949	030507-1	377	4.8516527	0.002653	0.159225
5.00	0.04949	030508-2	398	4.50079614	0.002513	0.173031
10.00	0.04949	030508-1	412	4.22979443	0.002427	0.181997
15.00	0.04949	030509-1	422	4.07453364	0.00237	0.18829

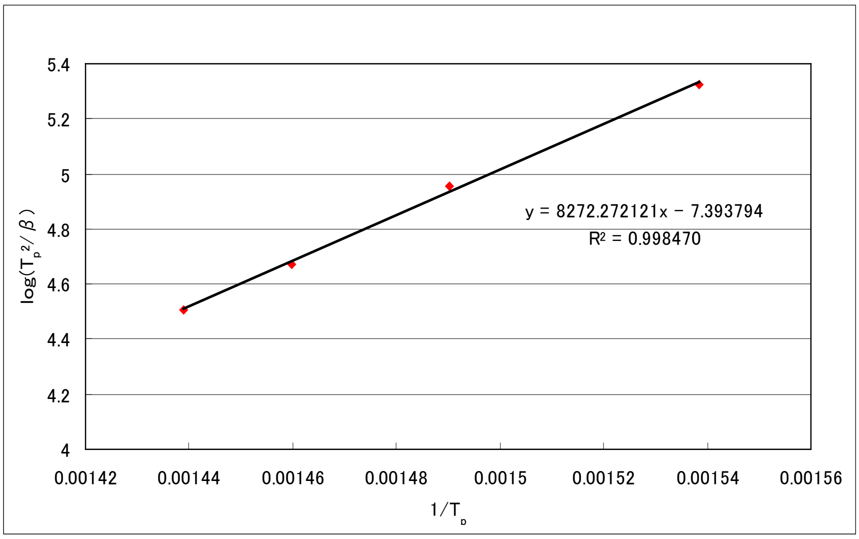

Figure 2: The Amemiya plot

Ed = 8272.27 × 2.303 × R (R=8.31 J/mol)
<u>Desorption energy (Ed) = 158 kJ/mol</u>

2. Results of adsorption heat calculation using Murakami-Tanwa equation

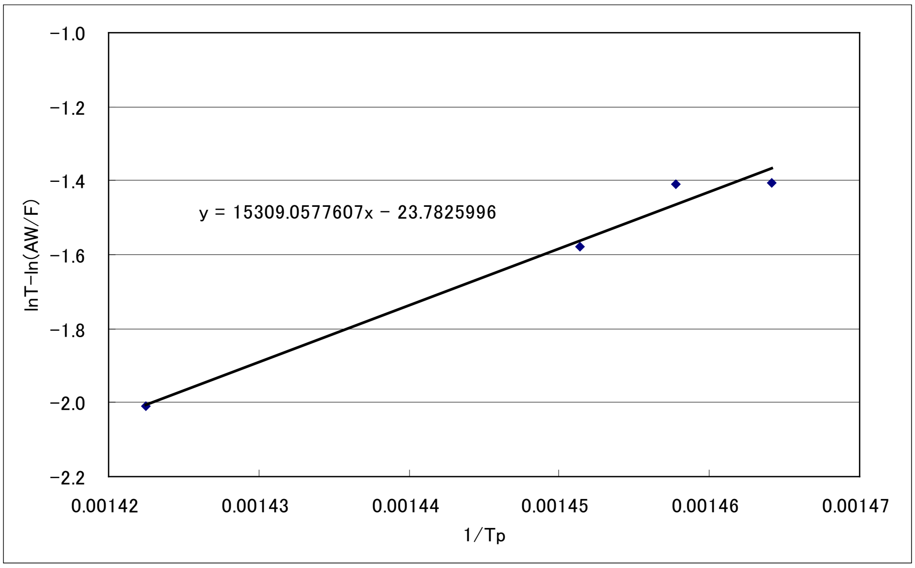

Fig. 3 Murakami-Niwa plot

Table 2 Numerical data

instrument	Sample weight	Tp/K	log(W/F)+3	1/Tp	F/ml	A0/mmol・g-1
BELCATII	0.03522	683	0.33	0.00146	75.05	0.990
BELCATII	0.03761	686	0.30	0.00146	75.38	0.938
BELCATII	0.06825	703	0.054	0.00142	77.26	0.990
BELCATII	0.04293	689	0.25	0.00145	75.71	0.981

ΔH = 15309.0578 × R R=8.31 J/mol
<u>Heat of adsorption (ΔH) = 127 kJ/mol</u>

References

1) Amenomiya, Y. and Cvetanovic, R.J., J. Phys. Chem. **67**, 144 (1963).
2) Cvetanovic, R.J. and Amenomiya, Y., Advan. Catal. **17**, 103 (1967).
3) Sawa, M., Niwa, M., and Murakami, Y., Zeolites. **10**, 307 (1990).
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5) Niwa, Catalysis, 33, 249 (1991).

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