B-AD-036

Influence of water vapor treatment for NH_3-TPD

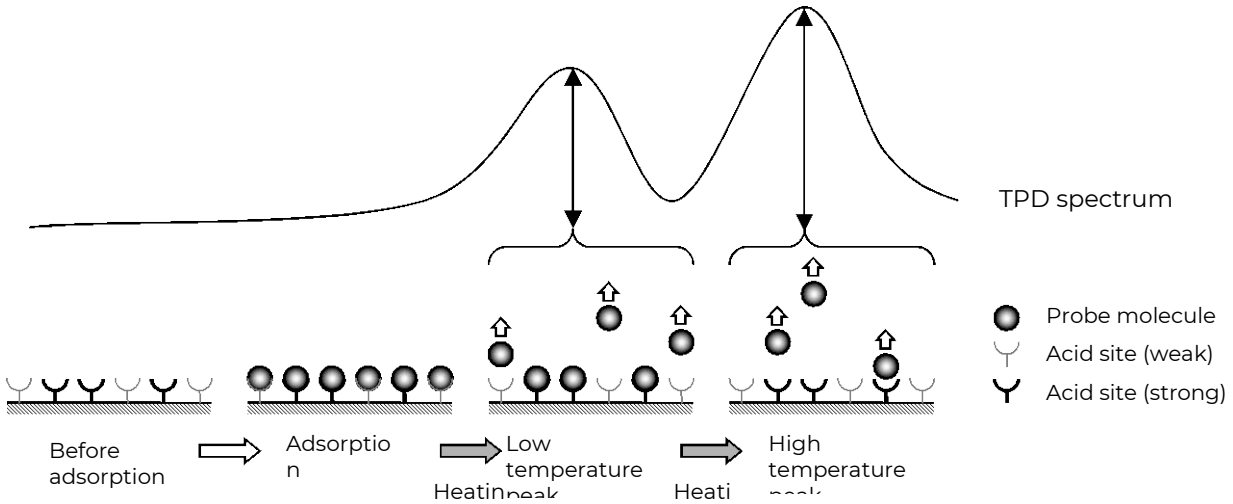
Introduction

Temperature programmed desorption of ammonia (NH_3-TPD) is commonly used to evaluate the acidity (acid amount, acid strength [heat of adsorption] of solid acid catalysts such as zeolites. In many cases, there are two peaks, *l*-peak (low temperature) and *h*-peak (high temperature) in the TPD spectrum.
The *l*-peak is derived from ammonia molecules which are adsorbed by hydrogen bonding on NH_4^+ cation on acid sites, and is not considered to indicate the acidity. However, in the case of zeolites with weak acidity, such as Y-type zeolites, the *l*-peak and *h*-peak overlap, making it difficult to evaluate acidity.
In this report, the procedure and precautions of NH_3 TPD measurement with steam treatment, which is considered to be effective to eliminate the *l*-peaks are described.

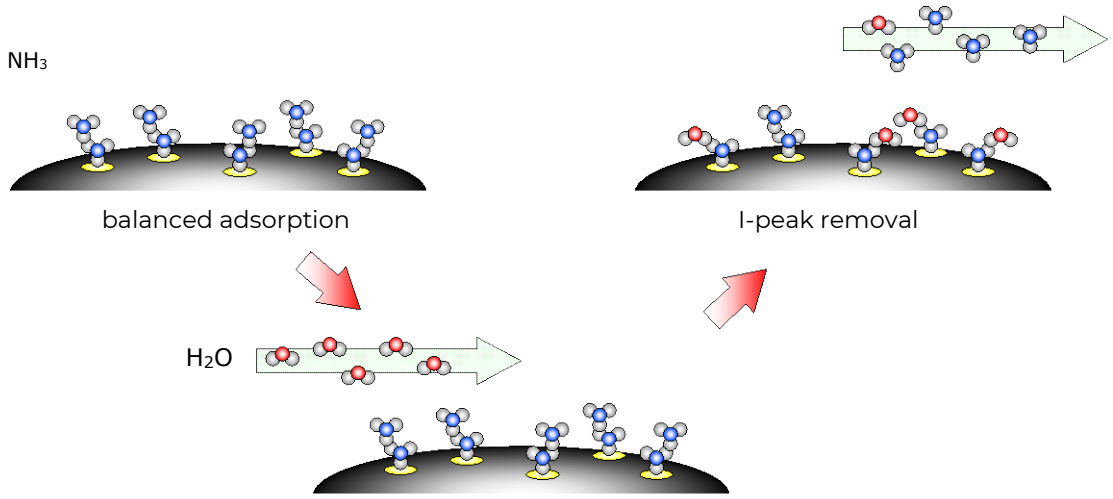
Experiment

1. Measurement principle

After the probe molecule (ammonia) is adsorbed onto the sample until it reaches equilibrium, the temperature of the sample is continuously increased in the carrier gas flow, and the desorbed probe molecule is measured.



However, as mentioned in the previous section, the *I*-peak is not an indication of acidic quality, but ammonia that is further hydrogen-bonded to the NH_4^+ cation. This can be removed by steam treatment after equilibrium adsorption.



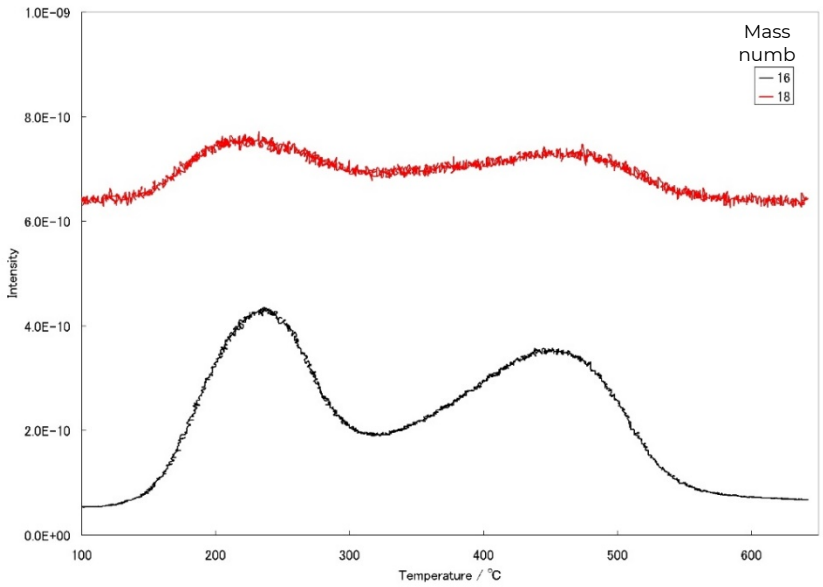
However, since zeolite adsorbs water in its pores, it is necessary to use a detector that can detect water and ammonia separately when measuring TPD. Also, since water vapor is introduced at high temperature, this method is not applicable to samples whose properties are changed by water vapor.
In this report, Q-mass (quadrupole mass spectrometer) is used to detect the desorbing ammonia at mass number 16. Mass number 17 was not used because of the peak at 17 can be affected by the desorption water.

2. Measurement of our NH_3-TPD reference sample under standard conditions

NH_3-TPD measurements were performed under the following conditions.

Pretreatment conditions

STEP	Gas	Flow rate (sccm)	Time (min)	温度 (°C)
1	He	50	50	500
2	He	50	60	500



3	He	50	1	100
4	He	50	10	100
5	NH_3	50	30	100
6	He	50	15	100

Measuring equipment : BELCAT II + BELMASS
Sample : MFI [990-00006-0-0], 50 mg
Temperature ramp rate and target temperature : 10°C/min, 610°C
Adsorption gas : NH_3/He 5%

3. Measurement of our NH_3-TPD reference sample after water vapor treatment

NH_3-TPD measurements were performed under the following conditions.

Pretreatment conditions

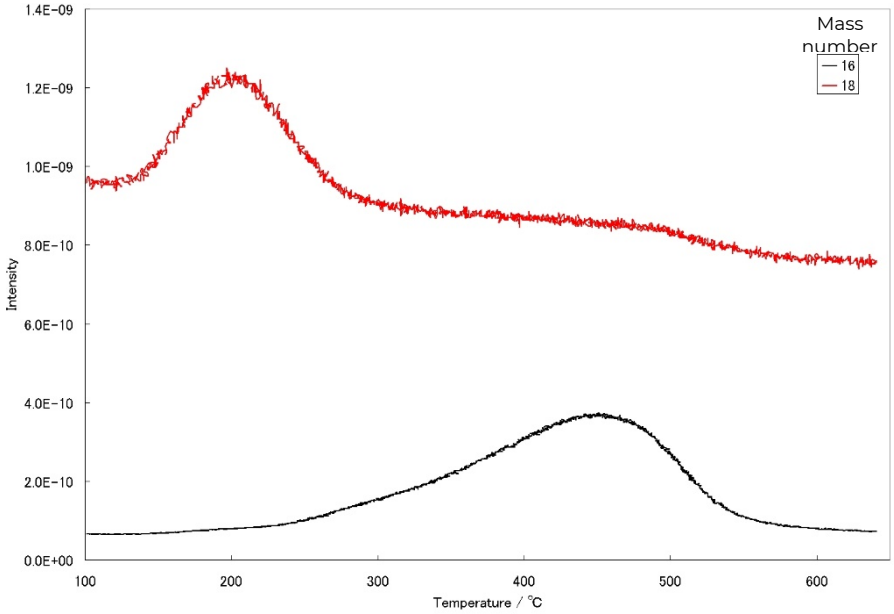
STEP	Gas	Flow rate (sccm)	Time (min)	温度 (°C)
1	He	50	50	500
2	He	50	60	500
3	He	50	1	100
4	He	50	10	100
5	NH_3	50	30	100
6	He	50	60	100
7	He+H_2O	50	30	100
8	He	50	30	100

Measuring equipment: BELCAT II + BELMASS
Sample: MFI [990-00006-0-0], 50 mg
Temperature ramp rate & target temperature: 10°C/min, 610°C
Adsorption gas: NH_3/He 5%
Water vapor treatment: He bubbling (room temperature)

The comparison of NH_3 TPD spectrum with and without steam treatment are shown.

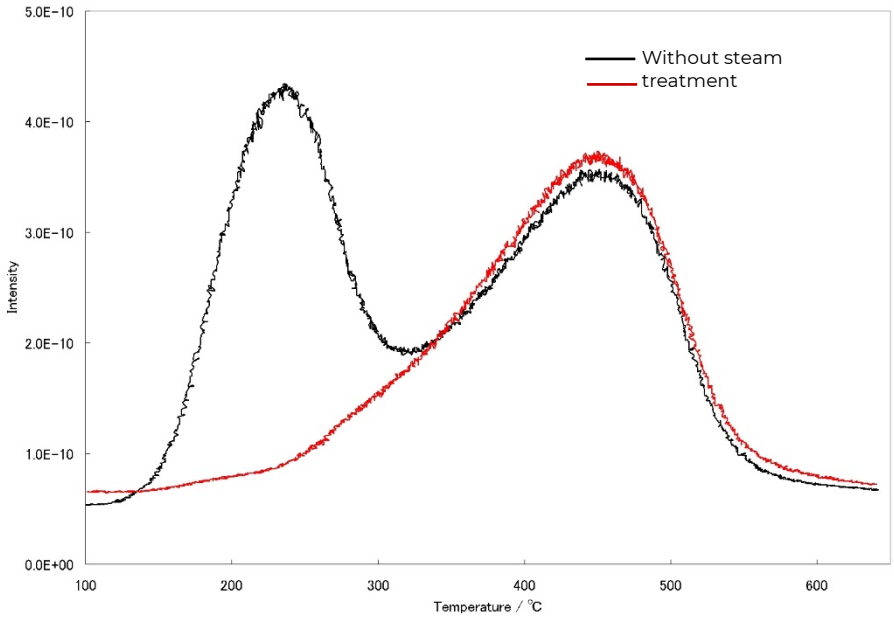
Result and Discussion

In the NH_3-TPD measurement of solid acid catalysts such as zeolites, the usefulness of



steam treatment was investigated in order to remove the *l*-peak. It would be more effective in the case that *l*-peak and *h*-peak are overlapped.

According to Ref 1), for the steam treatment, by repeating the sample cell evacuation and the steam introduction, the steam treatment was performed. However, the catalyst analyzer [BELCAT II] is a normal-pressure dynamic flow type equipment, so water vapor of saturated vapor pressure at room temperature under atmospheric pressure was introduced with inert gas by bubbling method.
The experimental results show that steam treatment almost completely eliminates the *l*-peak and leaves the *h*-peak shape almost unchanged, indicating that steam treatment in NH_3-TPD measurement is very effective for eliminating the *l*-peak and examining the *h*-peak in detail.



To perform NH3-TPD measurement with [BELCAT II], the vapor option and a quatdupole mass spectrometer [BELMASS] is necessary.

1) H.Igi, N.Katada, and M.Niwa, Proc. 12th Intl. Zeol. Conf. p.2643 (1999)

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