Quantifying Zeolite Acidity with Basic Probe Molecules: TPD Techniques with AMI Chemisorption Systems

1. Background

Temperature-programmed desorption (TPD) of basic probe molecules is a widely used technique for characterizing the acid properties of zeolites. By adsorbing a base onto the zeolite surface, then linearly increasing the temperature under inert gas flow, the desorption of the base can be monitored.[(1)]

Quantitative analysis of the desorbed species provides information about:

- ✓ Extrinsic acidity - number of acid sites
- ✓ Intrinsic acidity - acid strength, based on desorption temperature

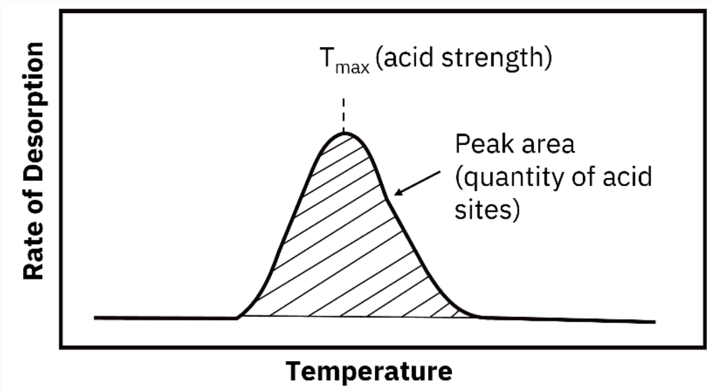


Figure 1: Graphical representation of TPD plot with basic probe molecules

This approach allows both parameters to be evaluated in a single experiment. The area under the desorption peak corresponds to the quantity of acid sites, while the desorption peak temperature (T_{max}) reflects the strength of those sites, shown in Figure 1. Higher desorption peak temperatures indicate strong acid-base interactions resulting from stronger acid sites.[(2)]

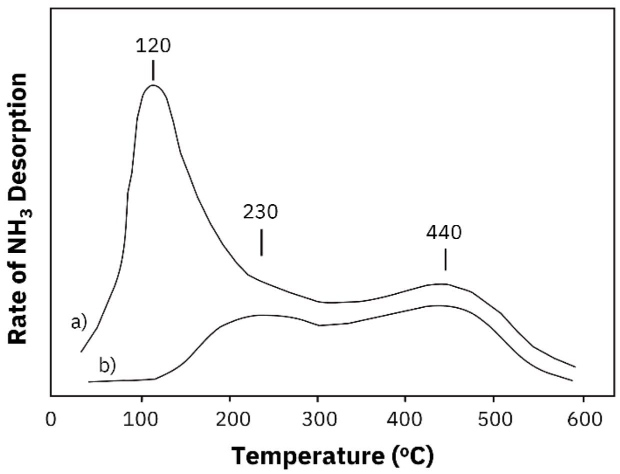


Figure 2: NH_3-TPD plots with sample a) showing physisorbed (120 °C) and chemosorbed (230, 440 °C) NH_3 and sample b) which shows only chemisorbed (230, 440 °C) NH_3

2. Common Probe Molecules

2.1 Ammonia

Ammonia (NH_3) is the most common probe due to the small kinetic diameter (0.26 nm), allowing access to virtually all acid sites. NH3 also has strong adsorption on sites of varying strength, and thermal stability over a broad temperature range. Because NH3 strongly adsorbs on all acid sites, it is useful for measuring the total acidity but cannot differentiate between different types of acid sites (Brønsted vs Lewis acids).

Ammonia desorption is typically observed in two distinct regions, shown in Figure 2:

- ✓ Peaks <150°C - Physically adsorbed ammonia (physisorption). This signal can be minimized by conducting adsorption at elevated temperatures (~100°C).

- ✓ Peaks between 200 and 500°C - Chemisorbed ammonia on acid sites. Multiple peaks may appear, reflecting a distribution of acid strengths.

For H-Y zeolite catalysts, acid strength can determine catalytic activity. This is shown in Figure 3, where the highest ammonia desorption temperature correlated with the best cracking activity of *n*-pentane, as shown by turnover frequency (TOF) data.

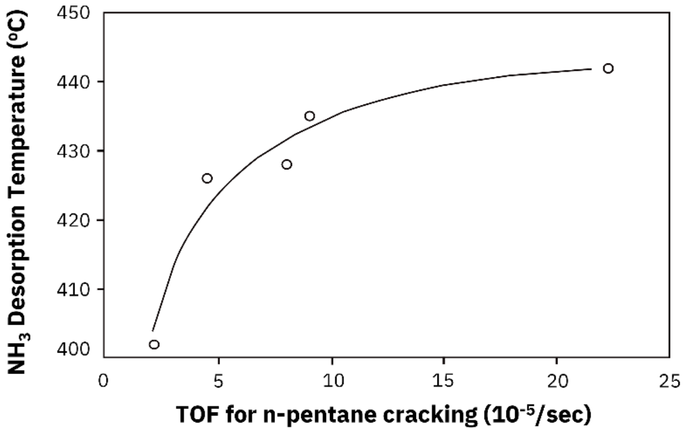


Figure 3: Correlation between NH_3 desorption temperature from H-Y zeolite catalyst and turnover frequency (TOF) for cracking of n-pentane

2.2 Pyridine and other bases

Pyridine (C_5H_5N) is a weak base that can adsorb on medium to strong acid sites, but not weak acid sites. Additionally, the molecule is bulky and cannot enter the small pores present in zeolites. However, pyridine adsorbed on a surface acid site is infrared (IR) active, with distinct IR bands that distinguish between pyridine attached to a Brønsted or Lewis acid site. Therefore, pyridine adsorption coupled with IR is commonly used in tandem with NH_3-TPD to gain a full understanding of zeolite acidity.

A recent study by Poreddy et al. combined pyridine diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments with NH_3-TPD to study the acidity of Mn/Zn/HY catalysts.(3) NH_3-TPD experiments were conducted on varying ratios of Mn/Zn on HY support, and the authors identified three desorption regions:

- ✓ Weak acid sites (150 – 250 °C)
- ✓ Medium acid sites (300 – 400 °C)
- ✓ Strong acid sites (450 – 550 °C)

The catalysts with increased Mn content were observed to have the most intense desorption peaks in the strong acid region.

Pyridine-DRIFTS was performed to understand the Brønsted and Lewis acid sites. After dosing pyridine onto the material, the molecule was protonated by Brønsted acid sites (Al-OH-Si) and exhibited a distinctive C-C stretch around 1550 cm^{-1}. When adsorbed onto a Lewis acid (Al ions), the surface pyridine molecule was identified by a band between 1445 – 1460 cm^{-1}. The characteristic IR peak areas were then used to calculate the ratios of Brønsted/Lewis acid sites for each catalyst. They observed that the Brønsted/Lowry acid site ratios decreased after either Mn or Zn was added, suggesting that metal addition influenced overall HY acidity.(3)

In addition to NH_3 and pyridine, a variety of bases can be employed depending on acid strength and pore accessibility, some of which are shown in Figure 4.(4,5)

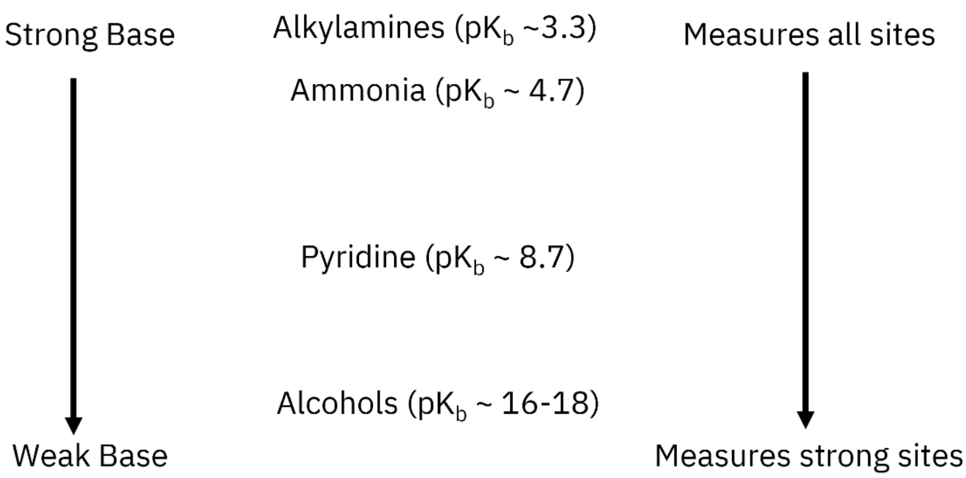


Figure 4: Basic probe molecules used in TPD to measure acidity

2.3 Practical Considerations

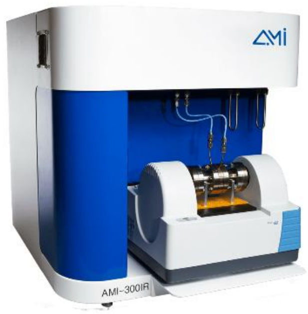
- ✓ Adsorption Temperature - Elevated temperatures reduce physisorption artifacts.
- ✓ Adsorption Time - Sufficient to ensure pore diffusion and full surface coverage.
- ✓ Reaction Risk - For strong acid sites, probe molecules may undergo side reactions. Selection should consider thermal and chemical stability.

3. Conclusions

Temperature-programmed desorption (TPD) of basic probe molecules is a powerful and flexible technique for characterizing the acidity of zeolites and related materials. By selecting the appropriate adsorbate and optimizing adsorption conditions, users can reliably quantify both the number and

AMI 300

- ✓ Flagship AMI model
- ✓ Fully automated chemisorption analysis
- ✓ Highly precise and customizable

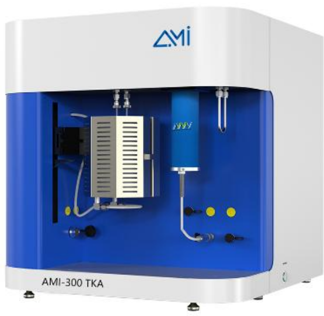


AMI 300 IR

- ✓ Automated chemisorption analysis with integrated FTIR spectrometer
- ✓ Real time catalyst surface analysis

AMI 300 HP

- ✓ Automated chemisorption analysis for pressures up to 100 bar
- ✓ Also functions as a high-pressure gas-phase reactor



AMI 300 SSITKA

- ✓ Automated chemisorption with integrated steady-state isotopic transient kinetic analysis (SSITKA)

*Figure 5: Highlighted features of **AMI 300** series of chemisorption analyzers*

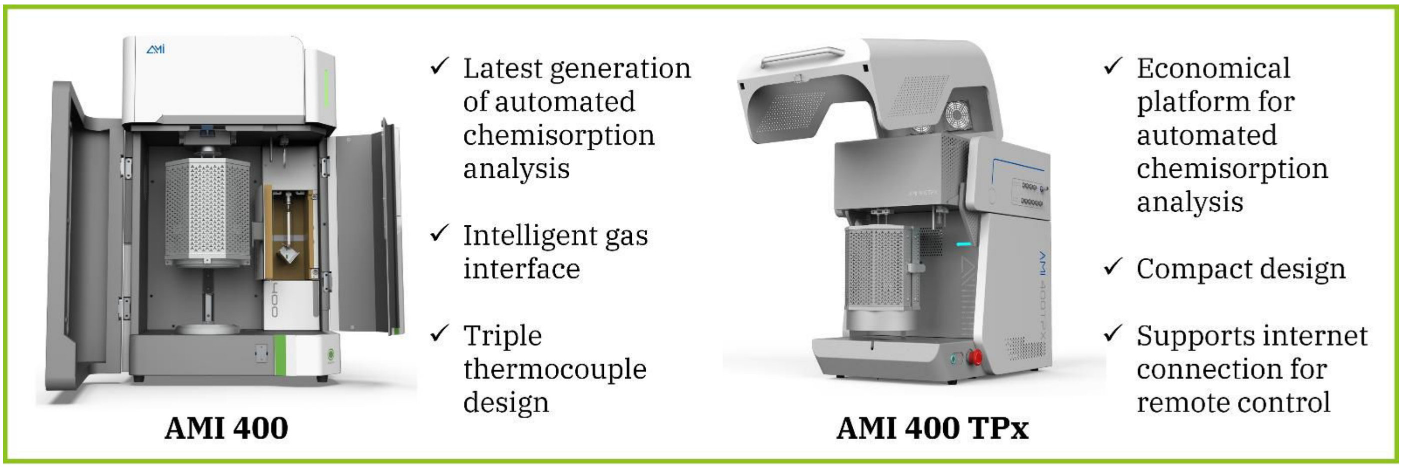


*Figure 6: Highlighted features of **AMI 400** series of chemisorption analyzers*

strength of acid sites—critical parameters that directly influence catalytic performance.

All **AMI chemisorption analyzers** are equipped to perform these TPD experiments with precision. Whether using ammonia for total acidity measurements or larger probe molecules like pyridine to selectively assess stronger or Brønsted versus Lewis acid sites, AMI systems offer the flexibility and control required for high-quality acidity analysis.

With robust temperature programming, sensitive detection options, and easy-to-use software, **AMI's chemisorption** product line, shown in Figures 5 and 6, enables researchers and catalyst developers to accurately measure acidity and apply these insights to optimize catalyst design, performance, and longevity.

4. References

(1) Ferneth, W. E.; Gorte, R. J. Methods for characterizing zeolite acidity. *Chem. Rev.* **1995**, *95*, 615-635.
(2) Védrine, J. C. Acid-base characterization of heterogeneous catalysts: An up-to-date overview. *Res. Chem. Intermed.* **2015**, *41*, 9387-9423.
(3) Poreddy, M. R.; Tewari, K.; Baddam, S. R.; Caiola, A.; Jiang, C.; Robinson, B.; Palanki, S.; Wang, Y.; Hu, J. Manganese and zinc supported on zeolite (SiO_2/Al_2O_3 = 5.1) catalysts for microwave-driven dehydration of ethanol to ethylene. *ACS Sustainable Chem. Eng.* **2025**, *13*, 19319-19327.
(4) Yiu, H. H. P.; Brown, D. R.; Barnes, P. A. Mesoporous solid acid catalysts: Relationship between amine TPD data and catalytic activities. *Catal. Lett.* **1999**, *59*, 207-211.
(5) Kwak, J. H.; Lee, J.; Szanyi, J.; Peden, C. H. F. Modification of the acid/base properties of γ-Al_2O_3 by oxide additives: An ethanol TPD investigation. *Catal. Today*, **2016**, *265*, 240-244.