Quantifying Zeolite Acidity: TPD Techniques with AMI

Introduction

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.

Quantitative analysis of the desorbed species provides information about:

- **Extrinsic acidity** (number of acid sites)
- **Intrinsic acidity** (acid strength, based on desorption temperature)

This approach allows both types of acidity to be evaluated in a single experiment (Figure 1).

Principles of TPD for Acidity Measurement

The **area** under the desorption peak corresponds to the *quantity* of acid sites, while the **peak temperature (T_{max})** reflects the *strength* of those sites.

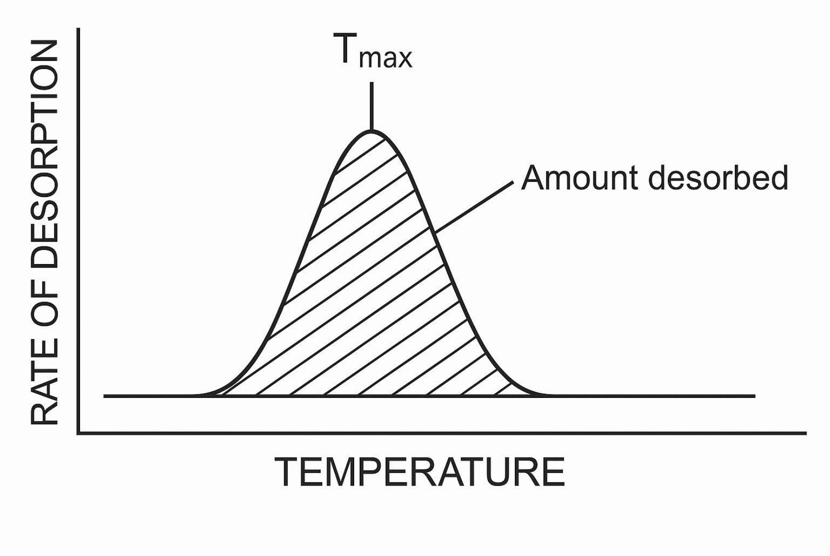

Figure 1. TPD experiment: T_{max} reflects acid strength (intrinsic acidity); peak area reflects number of acid sites (extrinsic acidity).

Common Probe Molecules

Ammonia (NH_3) is the most commonly used probe due to:

- Small kinetic diameter (0.26 nm), allowing access to virtually all acid sites.
- Strong adsorption on sites of varying strength
- Thermal stability over a broad temperature range

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Example: Ammonia TPD on H-Y Zeolite

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Desorption patterns typically show:

- **<150°C**: Physically adsorbed ammonia (physisorption). This signal can be minimized by conducting adsorption at elevated temperatures (~100°C).
- **200–500°C**: Chemisorbed ammonia on acid sites. Multiple peaks may appear, reflecting a distribution of acid strengths.

Literature Example

Zi et al. [1] observed that increasing the Si/Al ratio in H-Y zeolites resulted in a stronger high-temperature desorption peak, indicating a higher number of acid sites.

Shakhtakhtinskaya et al. [2] correlated desorption signals between 600–900 K (327–627°C) to Brønsted acid sites, which disappeared upon dehydroxylation.

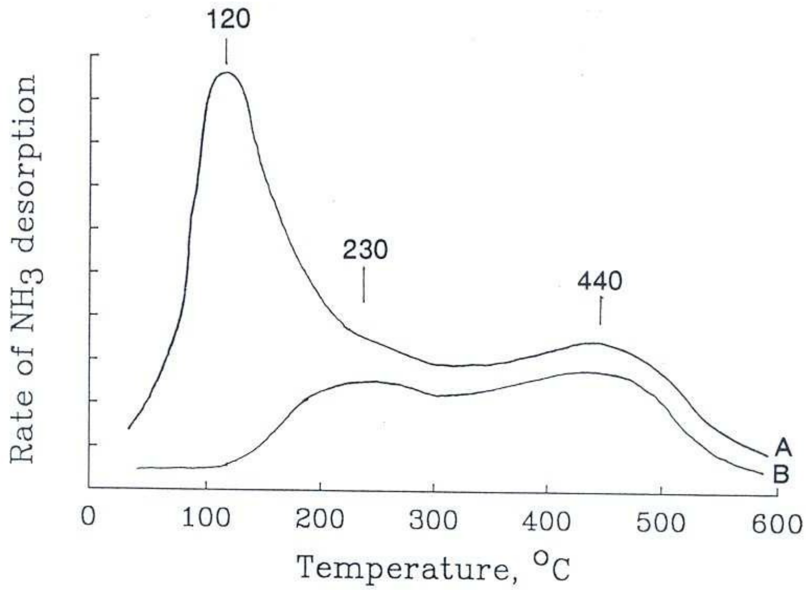

Figure 2. Typical TPD pattern of ammonia from H-Y zeolite. A: ammonia sorbed at room temperature; B: ammonia sorbed at 100°C.

Correlating Acidity with Catalytic Activity

TPD profiles not only reveal the number and strength of acid sites but also provide predictive insight into catalytic activity. In many systems, stronger desorption peaks (higher Tmax) correlate with increased activity in acid-catalyzed reactions such as cracking, alkylation, or isomerization. These correlations can guide formulation screening and performance optimization.

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Example

TPD provides quantitative information about acid site density, which can be directly linked to catalytic performance. For example, in the case of H-Y zeolite catalysts used in hydrocarbon cracking, knowing the number of desorbed ammonia molecules enables calculation of acid site concentration. When combined with independent measurements of reaction rate (e.g., n-pentane cracking), this allows researchers to calculate turnover frequency (TOF) — a metric that normalizes catalytic activity to the number of active sites, providing a more meaningful comparison across samples [3].

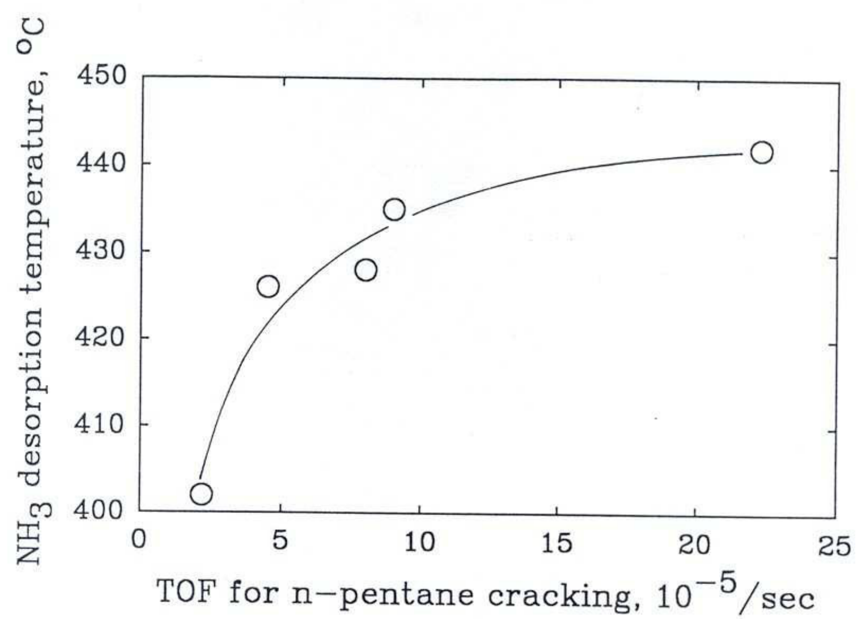

Figure 3. Correlation between n-pentane cracking TOF and peak ammonia desorption temperature (Tmax), illustrating how stronger acid sites can enhance per-site catalytic activity.

Alternative Probe Molecules

While ammonia effectively measures total acidity, other probes offer selectivity. Pyridine, for example, targets stronger acid sites and, when combined with IR spectroscopy, distinguishes Brønsted from Lewis acidity. AMI systems can perform pyridine TPD, but Brønsted/Lewis differentiation requires in situ IR (e.g., DRIFTS), not included in standard setups. Researchers requiring Brønsted/Lewis site discrimination may opt for custom AMI systems coupled with third-party IR detectors.

Pyridine Considerations: 1) binds to Brønsted and Lewis sites 2) IR needed for site-type resolution [4,5] 3) Careful control of temperature/time ensures full adsorption, especially in large-pore zeolites like mordenite [6].

Other Probes

A variety of bases can be employed, chosen based on acid strength and pore accessibility.

Table 1. Common Probe Bases for Acidity TPD

Strong Base	NH3	Measures all Sites
↓	Pyridine	↓
	Butylamine	
	Methylphosphines	
	Water	
	Alcohols	
	Phenol	
	Alkanes	
Weak Base	Alkanes	Measures Strong Sites

Note: Weak bases are generally used to probe only the strongest acid sites

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.

Summary

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

All AMI chemisorption analyzers are equipped to perform temperature-programmed desorption (TPD) experiments with precision. Whether using ammonia for total acidity measurements or larger probe molecules like pyridine to assess stronger acid sites, AMI systems provide the flexibility, gas handling, and temperature control needed for high-quality acidity analysis. While pyridine adsorption can offer some selectivity, distinguishing Brønsted from Lewis acid sites requires complementary infrared spectroscopy (e.g., DRIFTS), which can be used in conjunction with AMI's temperature-programmed capabilities.

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

References: While many foundational studies in acidity characterization date to the 1980s, their relevance remains unchanged in modern zeolite research and commercial catalyst evaluation.

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