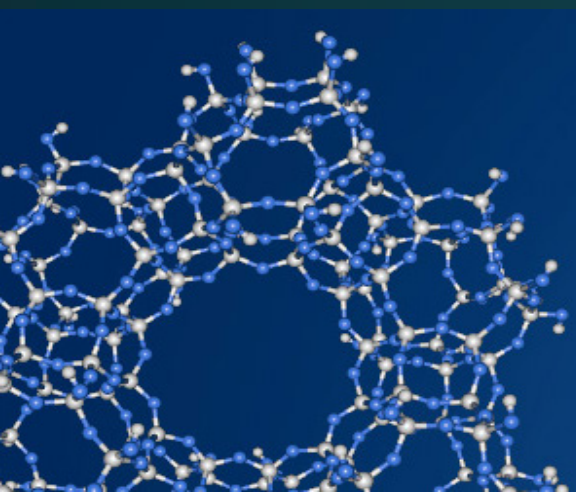
micromeritics®
a Malvern Panalytical company

# AMMONIA-TPD HEAT OF DESORPTION OF ZEOLITES USING CHEMISORB AUTO



**Zeolites and Their Importance in Catalysis and Adsorption**

Zeolites are a class of crystalline microporous aluminosilicates characterized by a three-dimensional framework of corner-sharing $SiO_4$ and $AlO_4$ tetrahedra. The substitution of silicon by aluminum in the framework generates a net negative charge, which is compensated by extra framework cations such as H+, Na+, or other metal ions. This unique framework composition gives rise to well-defined pore systems with uniform pore sizes in the range of molecular dimensions (typically 0.3–1.0 nm), making zeolites highly effective molecular sieves and shape-selective materials.

Because of their high surface area, regular pore architecture, and tunable chemical composition, zeolites have found widespread application in industrial processes. Their ability to selectively adsorb, transform, or exclude molecules based on size, shape, and polarity underlies many of their technological uses. Importantly, zeolites can be synthesized with a wide variety of framework topologies and silicon-to-aluminum ratios, allowing their catalytic, acidic, and adsorption properties to be tailored for specific applications.

Zeolites are among the most important solid catalysts used in the chemical and petrochemical industries. In particular, Brønsted acid zeolites play a central role in hydrocarbon processing reactions such as fluid catalytic cracking (FCC), hydrocracking, alkylation, isomerization, and methanol to olefins (MTO) conversion. The strong acidity arising from proton-compensated framework aluminum atoms enables efficient C–C bond rearrangement and cleavage reactions.

## Role of adsorption and desorption characterization

Characterization techniques based on adsorption and desorption, such as temperature-programmed desorption (TPD), are particularly important for probing the energetics and heterogeneity of zeolite surfaces. By monitoring the desorption behavior of probe molecules (e.g., ammonia, hydrocarbons, or CO), it is possible to assess:

- The number of accessible adsorption sites.
- The strength of interaction between adsorbates and the zeolite framework.
- Different types of adsorption sites are associated with different local structural environments.

Such information is critical for understanding catalytic mechanisms, optimizing reaction conditions, and guiding rational zeolite design.

micromeritics®
a Malvern Panalytical company

# Introduction to Temperature-Programmed Desorption

Temperature programmed desorption (TPD) is a thermal analysis technique in which a solid is saturated with a certain adsorbate at near room temperature, then is desorbed at a controlled rate while desorbing species are continuously detected, typically using a thermal conductivity detector (TCD) or a mass spectrometer (MS). Desorption occurs when the supplied thermal energy overcomes the adsorbate–surface interaction, producing characteristic desorption peaks that reflect the energetics of surface binding.

One of the most important thermodynamic parameters extracted from TPD analysis is the heat of desorption (often approximated as the desorption activation energy, E_"des" ). The temperature at which a desorption peak appears reflects the energy required to overcome the adsorbate–surface bond: species that are more strongly bound to the surface desorb at higher temperatures, whereas weakly bound species desorb at lower temperatures. Consequently, TPD enables both qualitative and quantitative comparisons of adsorption strengths across different materials or surface sites.

Understanding the interactions between gas-phase molecules and solid surfaces is essential in heterogeneous catalysis, adsorption science, and surface chemistry. The heat of desorption provides a quantitative measure of the energy required to remove an adsorbate from a surface and is directly related to adsorption strength, surface site identity, and chemical bonding.

Because of its experimental simplicity and sensitivity to surface energetics, TPD is widely applied to:

- Catalyst active site characterization
- Acid–base site strength determination
- Comparison of adsorption strengths across different materials

This application note demonstrates the use of the temperature programmed desorption (TPD) method on a zeolite sample to illustrate the capability of the ChemiSorb Auto 2730 system to obtain information related to the heat of desorption.

## Temperature-Programmed Desorption Working Principle

The working principle of temperature-programmed desorption (TPD) involves several steps. The first is catalyst activation, which can be performed in various ways. For example, some catalysts require air flow for calcination, while others use hydrogen to reduce the material to its active form. However, most catalysts are simply degassed using an inert gas to remove moisture and surface contaminants. Activation must be temperature-controlled, especially in the case of zeolites, as high temperature can dehydroxilate the Brønsted-acid sites, and hence, the sample loses its acidity.

Once activated, the sample is cooled to the adsorption temperature, which varies depending on the material. After cooling, the sample is saturated with an adsorbate gas or vapor. The ChemiSorb Auto system offers two saturation methods: pulse saturation via the loop and continuous flow via the patented blending valve.

Pulse saturation allows users to determine the cumulative quantity of gas adsorbed at a specific temperature. This method resembles pulse chemisorption, where precise gas quantities are repeatedly injected until saturation is achieved. By integrating the peak areas, users can calculate the cumulative quantity of gas adsorbed consumed. However, this method may overestimate consumption due to physisorbed gas, making it less reliable for quantification. Its main advantage is ensuring that the sample is fully saturated.

In contrast, continuous flow saturation enables more accurate quantification of gas consumption, provided that a gas calibration is performed. The ChemiSorb Auto has a patented blending valve that can automatically carry out this calibration. The drawback of this method is that it does not indicate whether a sample is completely saturated prior to desorption. To address this, users can increase the saturation wait time to ensure complete saturation. This consideration is particularly relevant for systems such as Ni-supported catalysts during H2 adsorption, where insufficient equilibration can lead to incomplete chemisorption and affect the resulting desorption analysis.

After saturation, the sample undergoes purging, a critical step to remove any remaining physisorbed gas that could interfere with the baseline readings. This is typically achieved by flowing inert gas over the sample for an extended period of time.

Finally, the desorption step involves heating the sample at a linear ramping rate to induce desorption or surface reactions.

## Methodology

The following experimental setup was used to obtain the heat of desorption of the aluminosilicate zeolite framework ZSM-5 (CBV 5524). Deviation from these conditions could produce different results.

- **Instrument setting (activation):** The sample was degassed under a helium flow of 25 standard cubic centimeters per minute (sccm).
- **Temperature ramp:** The sample was heated to 550 °C at a ramp rate of 10 °C/min and held at this temperature for 30 minutes.
- **Cooling step:** The sample was then cooled to 120 °C, which served as the adsorption temperature.
- **Instrument setting (adsorption):** The helium carrier gas was switched to 10% $NH_3$/He to saturate the sample at a flow rate of 25 sccm for 30 minutes.
- **Instrument setting (purge):** The active gas was turned off and replaced with helium to remove physisorbed residues for 60 minutes.
- **Equilibration:** Prior to the desorption step, a stable baseline was established.
- **Data acquisition:** Data was recorded at a sampling interval of 1 second.
- **Temperature ramp (desorption):** The sample was heated linearly at a rate of 10 °C/min to a final temperature of 550 °C. After reaching the final temperature, the sample was held for 10 minutes to allow the signal to return to baseline before the analysis was terminated.

The analysis was performed eight times consecutively on the same sample using heating ramp rates of 2, 4, 5, 7, 10, 15, 20, and 30 oC/min. The eight analyses were performed automatically in a continuous sequence, with no pauses between runs.

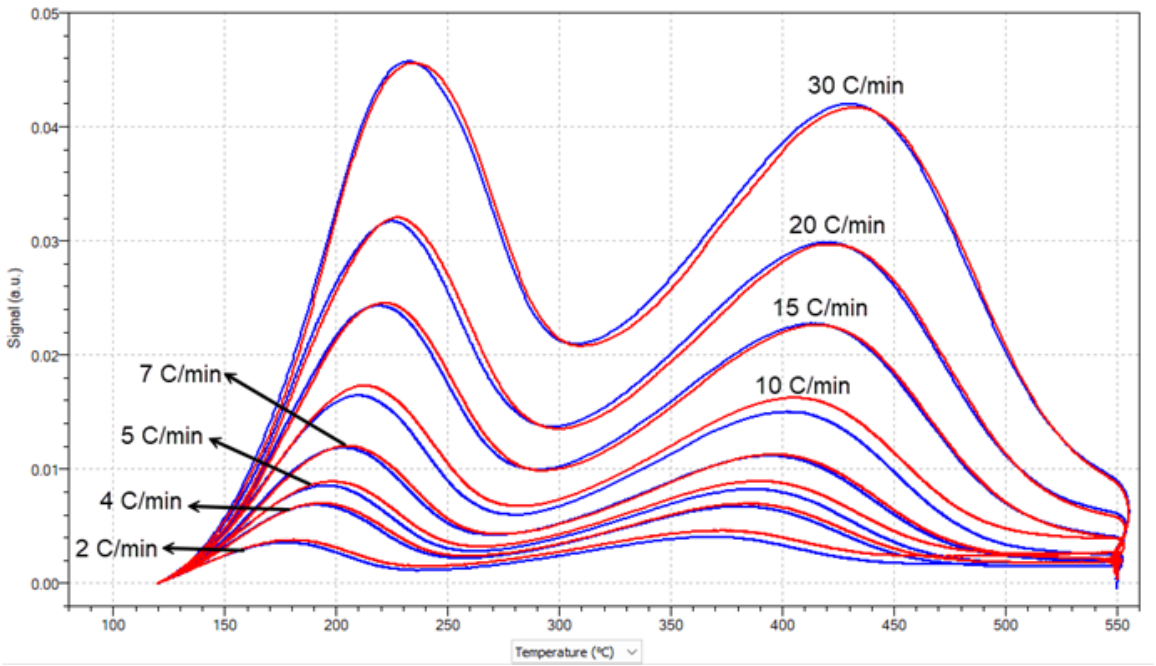



*Figure 1: Red line: Aliquot A / Blue line: Aliquot B. Ammonia TPD was performed on ZSM-5 using eight different heating rates. The measurements were carried out on the same catalyst material, using two separate aliquots of the sample.*

## Heat of Desorption Calculation

This procedure is used to determine first-order desorption kinetics, specifically the activation energy (often interpreted as the heat of desorption). A minimum of two experiments is required, although three experiments are typically performed for improved reliability. Each experiment must be conducted at a different linear heating ramp rate. The resulting peak temperature is analyzed using the Kissinger equation (Equation 1) by plotting $Ln(\beta/(T_p^2))$ vs $1/T_p$, from which the activation energy is obtained from the slope of the linear fit. The heat of desorption can then be calculated using (Equation 2).

**Kissinger equation:** $Ln(\beta/(T_p^2))=-E_d/(RT_p)+Ln((E_d Q)/RC)$
Equation 1: Kissinger equation

Where:

- $\beta$ — heating rate (K/min)
- $T_p$— Temperature at peak max (K).
- $E_d$— Heat of desorption (KJ/mol)
- R— Ideal gas constant (J/(K.mol))
- Q— The quantity adsorbed at saturation (cm3 at STP)
- C— A constant related to the desorption rate

**Heat of desorption:**
$E_d=S \times R$

Equation 2: Heat of desorption

Where:

- S — slope (K)

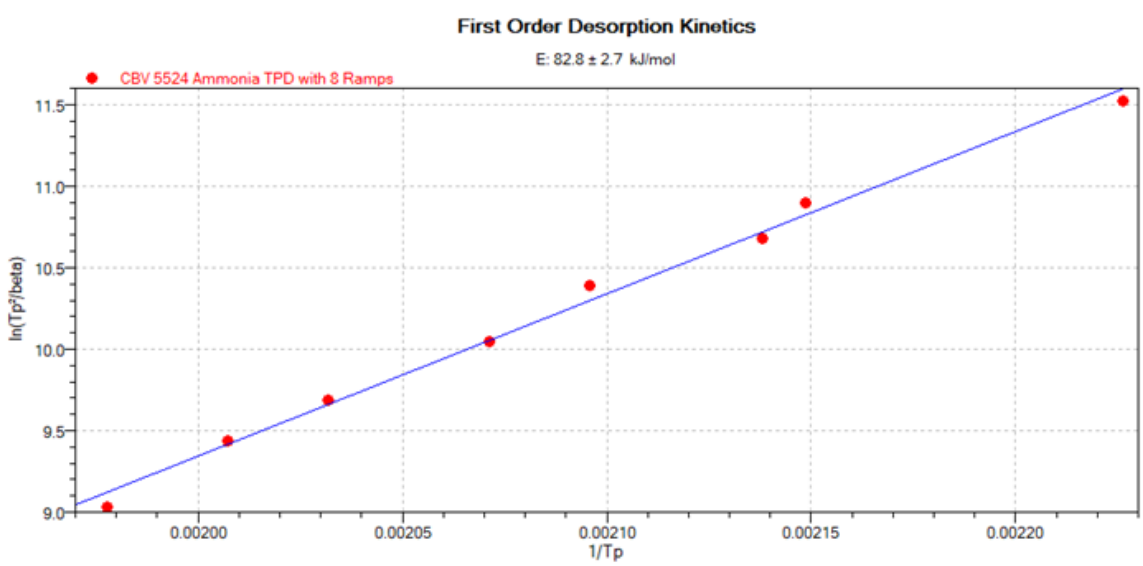



*Figure 2. First order desorption kinetics plotted from first desorption peak with different ramp rates on ZSM-5 from aliquot A.*

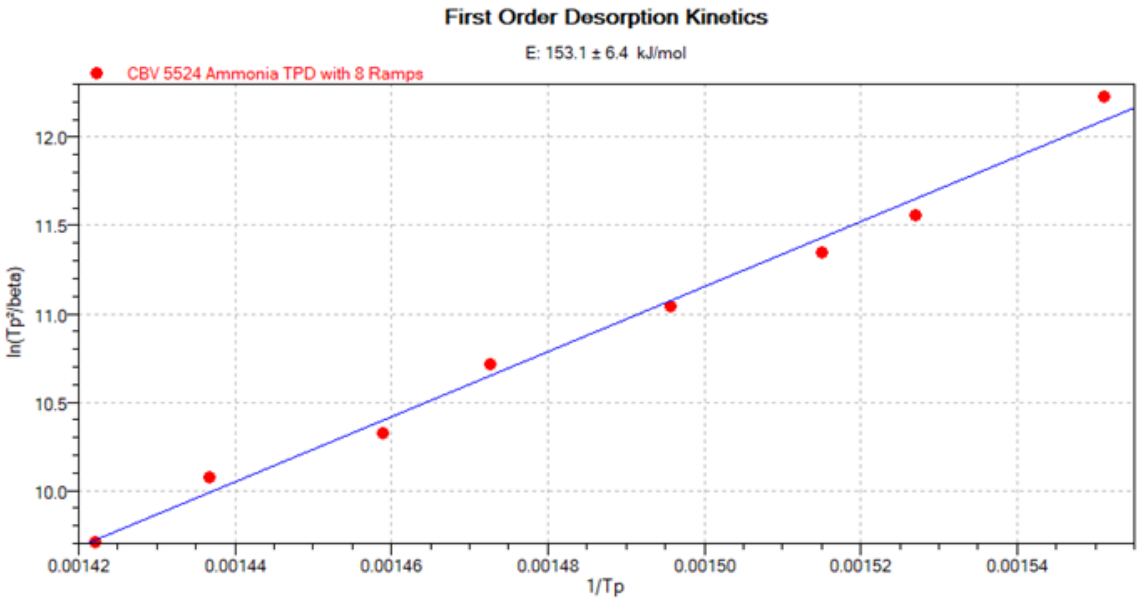



*Figure 3. First order desorption kinetics plotted from second desorption peak with different ramp rates on ZSM-5 from aliquot A.*

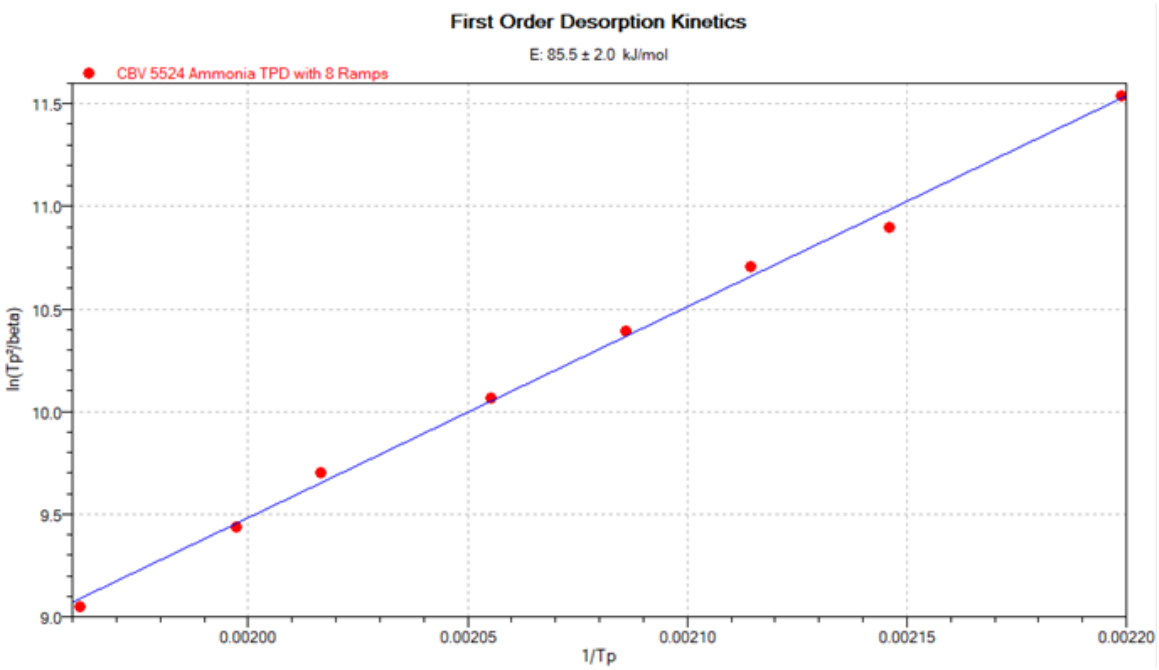



*Figure 4. First order desorption kinetics plotted from first desorption peak with different ramp rates on ZSM-5 from aliquot B.*

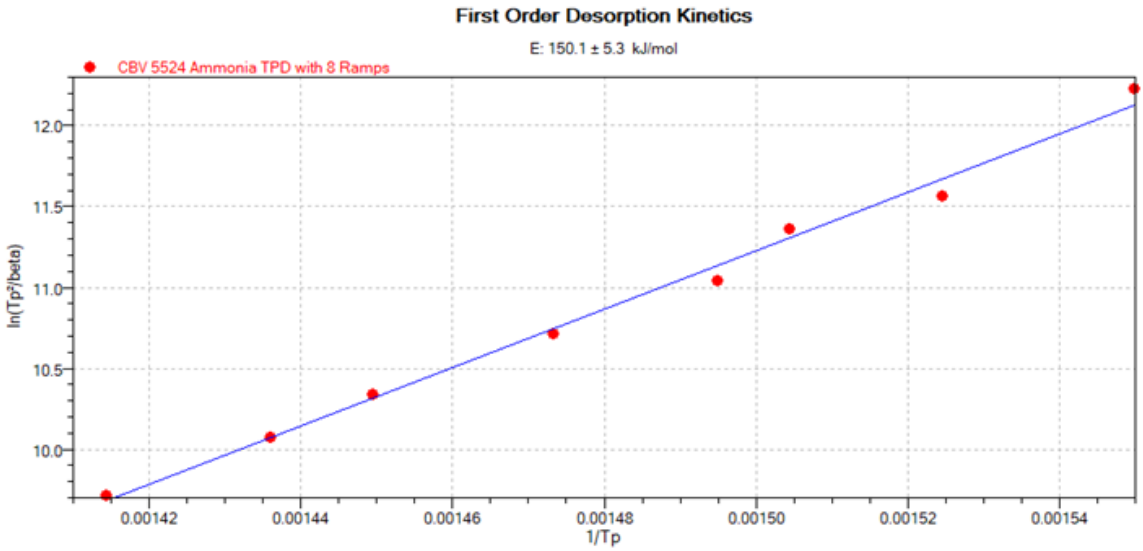



*Figure 5. First order desorption kinetics plotted from second desorption peak with different ramp rates on ZSM-5 from aliquot B.*

| | Edes (kJ/mol) | |
|---|---|---|
| | Aliquot A | Aliquot B |
| 1st Peak | 82.8 ± 2.7 | 85.5 ± 2.0 |
| 2nd Peak | 153.1 ±6.4 | 150.1 ± 5.3 |

*Table 1. Heat of desorption Edes determined from TPD analysis of ZSM-5 on two different aliquots.*

## CONCLUSION

Zeolites are essential materials in catalysis and adsorption due to their well defined pore structures, tunable acidity, and strong interactions with adsorbates. Characterizing these interactions is key to understanding and optimizing zeolite performance in catalytic and separation processes.

In this study, temperature programmed desorption (TPD) was used to investigate the desorption behavior of ammonia from ZSM 5. Distinct low  and high temperature desorption peaks were observed, corresponding to different acid site populations. By applying multiple heating ramp rates, the heat of desorption was determined, providing a quantitative assessment of adsorption strength on the catalyst surface. These results highlight the applicability of this TPD methodology on the ChemiSorb Auto for routine catalyst characterization, quality control, and comparative evaluation of acidic materials. The good agreement observed between independent sample aliquots demonstrates excellent reproducibility and reliability, confirming the ChemiSorb Auto as a robust and recommended instrument for routine catalyst characterization.

Overall, this work highlights the effectiveness of the ChemiSorb Auto 2730 system for TPD analysis and for extracting meaningful thermodynamic parameters. TPD remains a valuable and practical technique for probing surface energetics and supporting the design and optimization of zeolite based catalysts.

Grovewood Road, Malvern,
Worcestershire, WR14 1XZ,
United Kingdom

Tel. +44 1684 892456
Fax. +44 1684 892789

Copyright: © 2026 Malvern Panalytical