Altamira Instruments

Altamira Application Note

Acid Site Determination on a Zeolite Catalyst

The term *zeolite* was first used in 1756 by a Swedish geologist, Axel Cronstedt, who observed that rapidly heating a specific type of mineral produced large amounts of steam from water. From this initial discovery, we have today over 250 types of Zeolites that can occur naturally or be made synthetically. But the one common theme is that zeolites all have a porous structure that can accommodate a wide variety of cations, including Na^{+}, K^{+}, Ca^{2+}, $Mg^{2+,}$, among others. Having this variety of cations, in addition to a well-defined pore structure and adjustable acidity, make them highly active in a large variety of reactions. Today, Zeolites are one of the most widely used materials for catalysis and sorbents.

Synthetic zeolites, as other mesoporous materials, are widely used as catalysts in the petrochemical industry, specifically in catalytic cracking and hydrocracking. Zeolites confine molecules in small spaces, which causes changes in their structure and reactivity. The acidic forms of zeolites are often powerful solid acids facilitating a host of acid-catalyzed reactions, such as isomerization, alkylation, and cracking.

To help evaluate the applicability of a particular catalyst, Temperature Programmed Desorptions (TPD's) are commonly performed. TPD's of basic molecules from the surface of zeolites have been extensively used to measure their acid properties. The TPD experiment consists of sorbing a base molecule on the material of interest and, while flushing the surface with an inert gas, linearly ramping the temperature and measuring the desorption of the base. By quantitatively measuring the amount of base desorbed and noting the temperature(s) of desorption, information can be obtained on both the intrinsic and extrinsic acid properties in a single experiment. (1)

By far the most common type of TPD measurements on zeolites consists of ammonia desorption. Ammonia is a common adsorbate since it is accessible to all acid sites on the zeolite (kinetic diameter 0.26 nm), it is strongly adsorbed on sites of different acid strengths, and it is a stable molecule not susceptible to decomposition at elevated temperatures.

In the current study, we have used well-defined ZSM-5 catalysts with low aluminum content. ZSM-5 has a high silicon to aluminum ratio. Whenever a Si^{4+} cation is replaced by Al^{3+} cation, an additional positive charge is required to keep the material charge-neutral. With proton- (H^+) as the cation, the material becomes very acidic. Thus, the acidity is proportional to the Al content. So based on the TPD results and by determination of the amount of ammonia adsorbed, the uptake and the aluminum content can be determined.

Ammonia desorption from ZSM-5 generates multiple peaks from ca. 100°C to 500°C. (2), (3). Hence, determination of acid sites can be achieved by adsorbing ammonia at higher temperatures, thereby eliminating the physisorbed ammonia at lower temperature regimes. The current study uses this approach. Deconvolution of the TPD peaks provides the approximate ammonia uptake values.

Experimental

The catalyst used for this study was ZSM-5 from Acros Organics. The ICP-AES analysis of the sample yielded an aluminum content of 0.22 %, which approximates to 80 µmoles/gram of the catalyst.

TPD procedure:

The experiment was carried out using the Altamira Instruments AMI 200 catalyst characterization instrument equipped with a Thermal Conductivity Detector (TCD). The sample was first treated with helium from room temperature to 600°C. This was followed by adsorption of a 10% ammonia in helium mixture at 30°C. Then a stream of Helium gas was passed over the sample to remove any loosely held ammonia. This was followed by the TPD step under a carrier stream of helium and linearly ramping from 30°C to 600°C.

The same experiment was repeated by adsorbing ammonia at 75°C and 125°C and the TPD was carried out by linearly ramping from 75°C to 600°C and 125°C to 600°C under helium respectively. A 500µl sample loop was used to perform the pulse calibration procedure to determine the amount of ammonia adsorbed at the different adsorption temperatures.

Results

Figure 1 is the deconvoluted TCD signal of the TPD curve that was generated for the 30°C ammonia adsorption experiment. Table 1 gives the summary of the integrated areas under each deconvoluted peak and the corresponding ammonia uptake that was calculated in µmoles/gram of the sample. The highest temperature of each peak is also shown in the table.

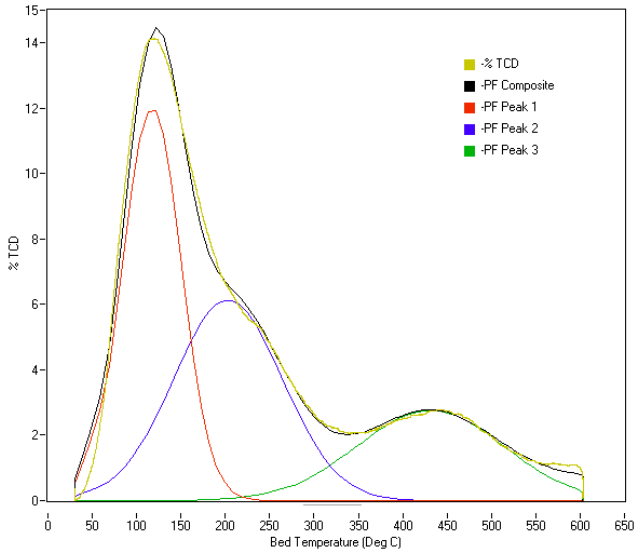

Figure 1*:* Peak deconvolution curves of the ammonia TPD for the 30°C adsorption

Table 1: Summary of integrated results of the TPD curve from Figure 1

Peak Number	Integrated Area	Uptake (µmoles/g)	Peak Temperature (°C)
Peak 1	29013	157	122
Peak 2	28006	152	220
Peak 3	17133	93	440

Figure 2 shows the mass spectral data generated during the TPD step for the 30°C adsorption experiment.

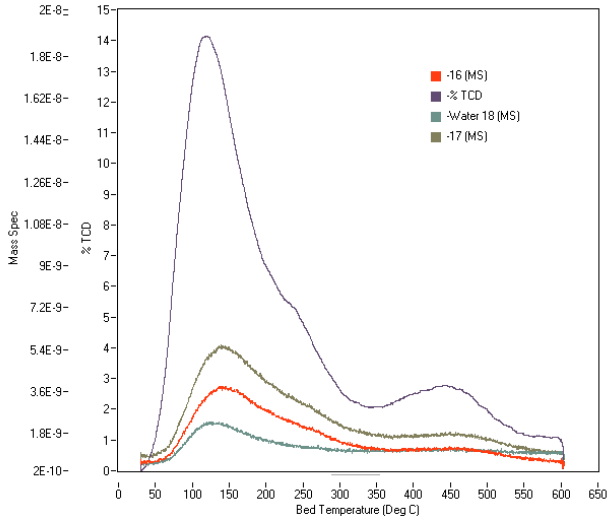

Figure 2: Mass spectral data during the TPD step for 30°C ammonia adsorption

Figure 3 is the deconvoluted TCD signal of the TPD curve that was generated for the 75°C ammonia adsorption experiment. Table 2 gives the summary of the integrated areas under each deconvoluted peak and the corresponding ammonia uptake that was calculated in µmoles/gram of the sample.

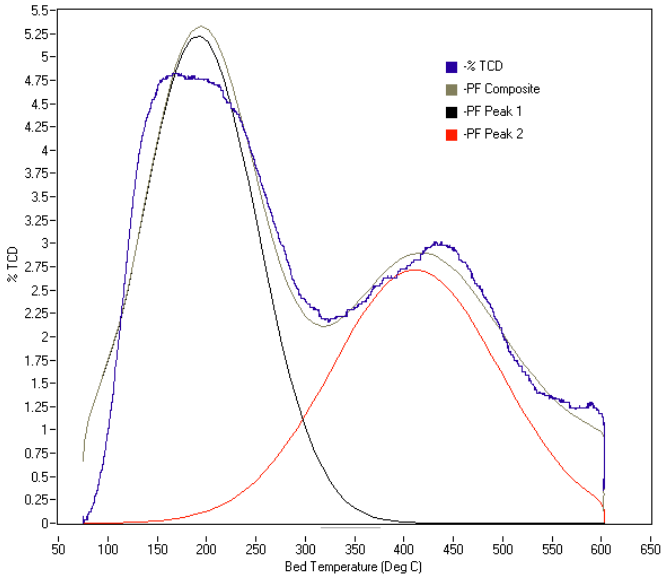

Figure 3: Peak deconvolution curves of ammonia TPD for the 75°C adsorption

Table 2: Summary of integrated results of the TPD curve from Figure 3

Peak Number	Integrated Area	Uptake (µmoles/g)	Peak Temperature (°C)
Peak 1	19987	115	180
Peak 2	17621	101	450

Figure 4 shows the mass spectral data generated during the TPD step for the 75°C adsorption experiment.

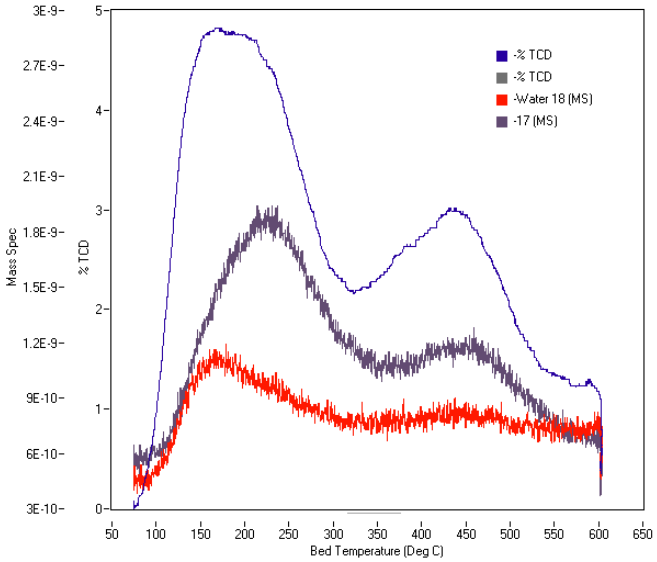

Figure 4: Mass spectral data during the TPD step for 75°C ammonia adsorption

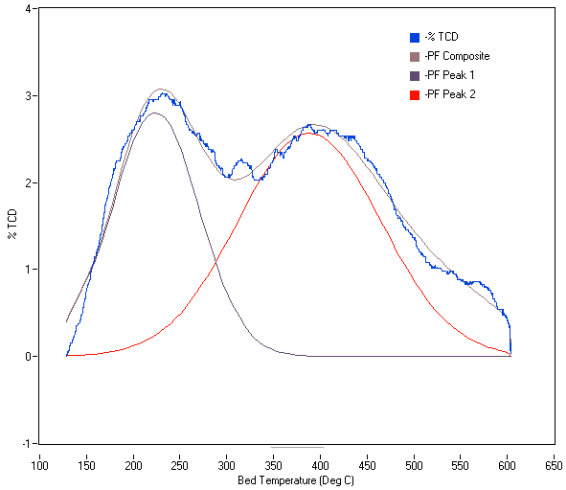

Figure 5. Peak deconvolution curves of ammonia TPD for the 125°C desoprtion

Figure 5 is the deconvoluted TCD signal of the TPD curve that was generated for the 125°C ammonia adsorption experiment. Table 3 gives the summary of the integrated areas under each deconvoluted peak and the corresponding ammonia uptake that was calculated in µmoles/gram of the sample.

Table 3

Summary of integrated results of the TPD curve from Figure 5

Peak Number	**Integrated Area**	**Uptake (µmoles/g)**	**Peak Temperature (°C)**
Peak 1	8157	45	235
Peak 2	14651	82	420

Figure 6 shows the mass spectral data generated during the TPD step for the 125°C adsorption experiment.

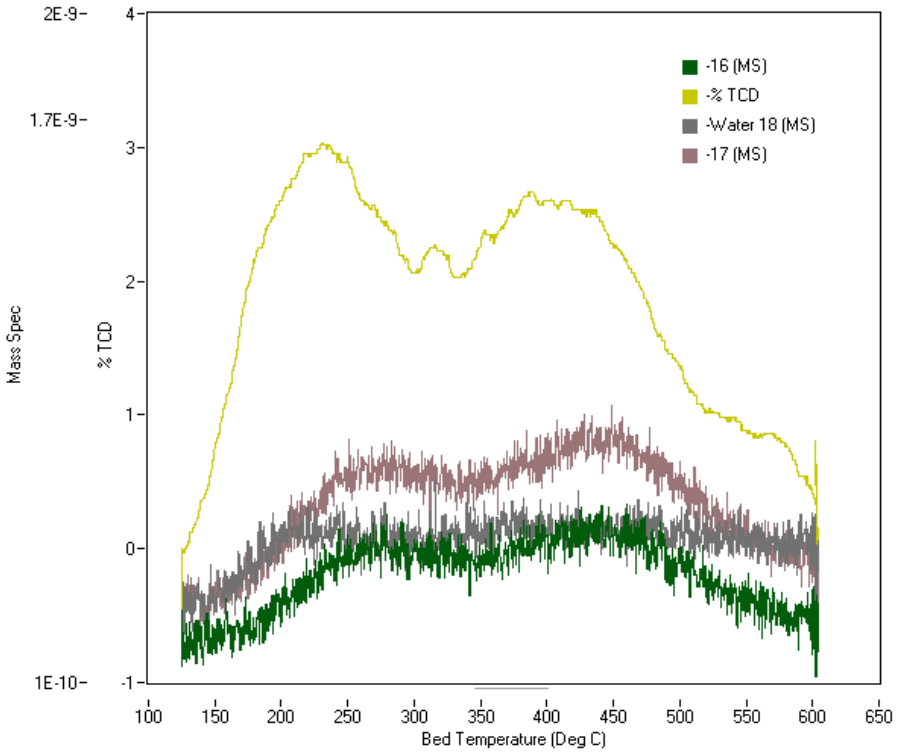

Figure 6: Mass spectral data during the TPD step for 125°C ammonia adsorption

Summary

Ammonia TPD patterns from ZSM-5 can exhibit multiple desorption peaks. The desorption signal observed below ca. 150°C corresponds to physically adsorbed ammonia. Physisorption can occur not only on the catalyst surface but also on various components of the experimental system. It can be virtually eliminated by conducting the sorption at elevated temperatures above 100˚C. The other desorption signals correspond to ammonia adsorbed on surface acid sites with multiple signals being discerned between 200 and 500°C. The nature of these signals, particularly the high temperature signals, can be directly related to the acidity of the catalyst.

Conclusion

Based on the experimental results conducted, it can be concluded that the peak near 450°C best agrees with the aluminum content. So if there is one acid site for every Al site, then an ammonia TPD is an excellent technique for measuring the acid sites.

The best way to determine acid sites is to carry the adsorption out at elevated temperatures to help eliminate the weakly held ammonia and then deconvolute the resulting signals and integrate to determine the highest temperature peak.

REFERENCES

(1) Measuring acidity in zeolites using TPD, Altamira Note 13, Vol. 3.2

(2) Characterization II, “Molecular Sieves”; H.G. Karge, J. Weitkamp.

(3) Characterization of catalyst acidity by microcalorimetry and temperature programmed desorption, S.B Sharma et al., Applied Catalysis A: General, 102 (1993), 253-265.

Altamira Instruments
149 Delta Dr
Pittsburgh, PA 15238
www.altamirainstruments.com
email: info@altamirainstruments.com
tel: +1-412-963-6385