

# Thermotitrimetric Characterization and Determination of Acidic and Basic Sites on Catalysts

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The catalytic activity of zeolites, aluminas, clays, and other materials is related to a great extent to the presence of ionic surface charges. It is therefore important to characterize the nature, number, strength, and distribution of acidic and basic sites of such materials, to assist in the evaluation of their catalytic activities, metal support, and binding energies.

Rabo studied the acidic sites on zeolite catalysts using thermometric titration.<sup>1</sup> Ghosh and Curthoys<sup>2</sup> employed an IR technique to measure Brønsted acid sites. Amines such as methylamine, n-butylamine (n-BA), and anilines have also been used in colorimetric determinations in conjunction with Hammett indicators,<sup>3,4</sup> but Deeba and Hall<sup>5</sup> have cast serious doubt on this approach, noting that Hammett indicators are unsuitable for studying Brønsted acid sites on zeolites.

Ghosh and Curthoys conducted a thermal study on the chemisorption of ammonia and n-BA on mordenites, concluding that zeolite surfaces are nonuniform, and that some of the active sites are stronger than others. A proportionately larger heat of absorption is obtained with stronger sites than with weaker sites. It was found that desorption occurs at 348–393K for weaker sites compared to 478–678K (the onset of zeolite decomposition) for stronger sites. Jacobs and Uytterhoven<sup>6</sup> determined that the hydrogen bonding of n-BA to the acidic site ceases above 623K.

Skeels and Flank<sup>7</sup> concluded that thermogravimetry produced similar results to IR. Brønsted sites represent proton acidity, with approximately two-thirds of the total acidity being due to the presence of H<sub>3</sub>O<sup>+</sup> or H<sup>+</sup>. Skeels and Flank found groups of sites of similar acidic strength by washing a ZSM-5 zeolite with NaCl solution, and determining the pK<sub>a</sub> in the washings by potentiometric titration, stopping their titrations at pH 10.

Because calorimetric studies had previously yielded important data on the properties of acidic sites, it was reasoned that enthalpimetric titration and calorimetric measurements may be techniques worthy of investigation when applied to catalytic materials. Thermometric titration offers a dynamic method of determining the relative strength of acidic and basic sites of zeolites, as well as other surface-active materials such as treated clays, carbon, and pigments. By using a sensitive, fast-response thermistor, titrations may be performed directly with the material under study in a nonaqueous environment, instead of using indirect aqueous techniques, such as those practiced by Skeels and Flank. Thermometric sensing relates to a fundamental chemical property of chemisorption. It was considered that the chemisorption behavior and quantification of acidic sites of different strength could be studied by titrating them directly with n-BA in a nonpolar solvent such as cyclohexane. Similarly, it was considered that trifluoroacetic acid (TFA) may be used to titrate basic sites directly.<sup>7</sup> Titration in nonaqueous media minimizes interference from residual acidic or basic ionic species not removed after the manufacturing process. While potentially capable of providing insight into the fundamentals of catalytic activity, thermometric titration finds its main application in

many industries as a process and quality control procedure due to its simplicity, robustness of operation, and speed. It was considered that it may find application as a tool for improving existing catalyst production processes and in the development of new products.

## Experimental

### Equipment

Thermometric titration was performed using the FACTS™ CE2000 (SANDA Corp., Philadelphia, PA). A buret delivers titrant at a constant rate into an insulated vessel, where the contents are stirred by a magnetic spin bar. A balanced thermistor (as an arm of a standard Wheatstone bridge) registers changes in temperature in the vessel. Signal amplification and derivatization are carried out, and data are transferred to a computer via an A/D board. Proprietary titration software enables operation of the buret, real-time display of the titration, data collection, and computation of results.

### Samples

Commercial catalysts in powder form were provided by manufacturers for evaluation. To eliminate the influence of water, all were dried for several hours in an evacuated desiccator with P<sub>2</sub>O<sub>5</sub> as desiccant.

### Reagents

Titrant for acidic sites was 2.5 M n-Butylamine. Twenty-five milliliters of n-Butylamine was diluted to 100 mL with dry cyclohexane.

Titrant for basic sites was 3 M TFA. Thirty milliliters of TFA was diluted to 100 mL with dry toluene.

### Titration procedure

The catalysts were weighed in amounts ranging from 1 to 3 g and rapidly transferred to the titration vessel, a small insulated flask provided with a lid assembly that also held the titrant delivery tube and the thermistor sensor. The catalysts were dispersed in accurately dispensed aliquots of dry solvent (cyclohexane for the determination of acidic sites and toluene in the case of basic sites). The use of accurately known volumes of solvent permits calorimetric measurements to be made (to determine such parameters as acidic or basic group bond strengths), and allows rapid qualitative comparisons between different catalysts. The

SANDA titration software enables the aliquoting of reagents prior to the titration using a spare buret module. A magnetic spin bar is provided.

The stirrer speed was adjusted to produce optimum mixing without splashing. The titration software provides for automatic balancing of the Wheatstone bridge circuit, and the titration commences automatically after the bridge is balanced. Titrant is added at a constant rate until the analyst determines that all endpoints have been found, or until a preset “titration stop” parameter is reached. This may be either a definite maximum preset volume of titrant or a preset first derivative voltage. In some experiments, a preset aliquot of titrant was added in a single, precise dose of predetermined volume.

Titration endpoints were determined from the negative peaks on the second derivative curve.

### Experimental series

Series 1: Three commercially available catalysts were titrated with 2.5 M n-BA and 3 M TFA, respectively, to determine the relative concentrations of acidic and basic sites. Masses of 1, 2, and 3 g of catalyst were titrated with each titrant.

Series 2: Samples of alumina catalysts of varying specific surface areas had been analyzed previously by a manufacturer for catalyst activity, as determined by the chemisorption of ammonia on acidic sites. The mass of ammonia sorbed was determined by thermogravimetric analysis (TGA). These samples were subjected to enthalpimetric analysis by treatment with a single 3.00-mL aliquot of 2.5 M n-BA, with the temperature increase observed.

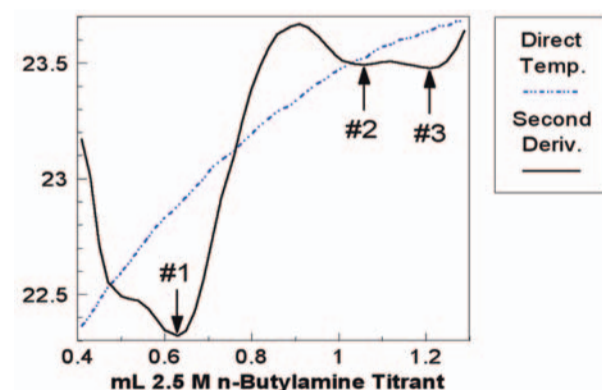


Figure 1 Typical thermogram of titration of acidic sites on a zeolite cracking catalyst with n-BA.

**Table 1** Temperature readings derived from Figure 1

Endpoint no.	Titer (mL)	Titer difference (mL)	Temperature (°C)	Temperature difference (°C)	Temperature rise/mL
Initial temperature of slurry (shoulder)			21.091		
1	0.517	0.517	22.635	1.544	2.986
2	0.626	0.109	22.880	0.245	2.248
3	1.057	0.431	23.525	0.645	1.497
	1.208	0.151	23.642	0.117	0.775

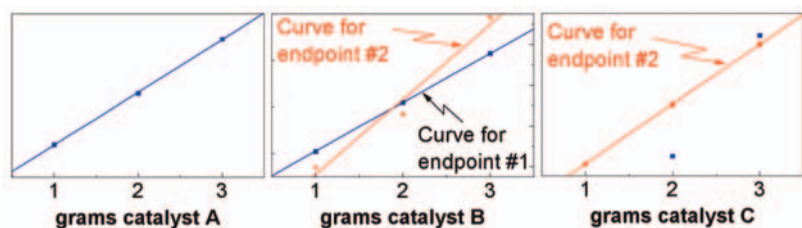


Figure 2 Titration of acidic sites on catalysts A, B, and C with 1 M n-BA, as a function of sample mass.

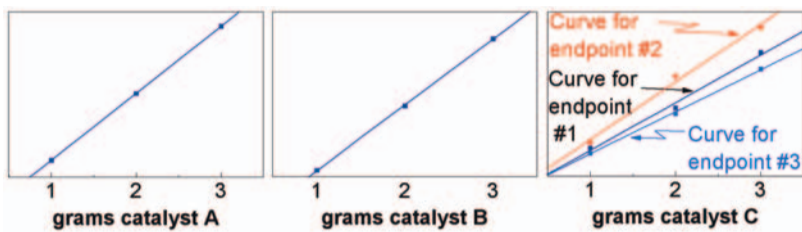


Figure 3 Titration of basic sites on catalysts A, C, and D with 3 M TFA, as a function of sample mass.

Series 3: Samples of zeolitic catalysts (faujasites and ZSM-5 zeolites) had been analyzed previously by the TGA method described in Series 2, and by the ammonia-TPD (temperature-programmed desorption) method. Both of these methods are used extensively by industry to evaluate the acid site strength of catalysts and their supports. The ammonia-TPD method involves ammonia sorption under a lengthy temperature-time regime, with temperature-dependent desorption of the ammonia being carried out after equilibration of the sample. A thermal conductivity mass flow cell is used to quantify the amount of ammonia sorbed.

Two thermometric titration techniques were evaluated with this experimental series. The first technique involved continuous addition of titrant at a fixed rate of 36  $\mu\text{L}/\text{sec}$ . The second technique involved punctuated addition of titrant, with a time delay between each addition to permit the system temperature to stabilize between additions. Punctuated addition sequences may be automated using SandaWin<sup>®</sup> titration software (SANDA Corp.). It was considered that comparison of the two titration techniques may provide insight into the role of pore diffusion in determining catalyst activity.

## Results

A typical titration thermogram is illustrated in Figure 1. A sample of a zeolytic cracking catalyst was suspended in cyclohexane, and the acidic sites titrated with 2.5 M n-BA. Titration data derived from Figure 1 are listed in Table 1.

The thermogram shows two curves: the direct temperature of the alumina slurry being titrated and the second derivative of this curve. Three distinct endpoints are visible, and an unresolved endpoint in the form of a “shoulder” prior to the first endpoint may also be observed.

Series 1: Effect of sample mass on titration of acidic and basic sites. Excellent linearity of endpoint response to increasing amounts of sample was found. In a number of cases, multiple endpoints were determined, and two calibration curves are illustrated (Figures 2 and 3). In the case of determination of the acidic sites, a first endpoint for a sample mass of 1 g of catalyst C was not determined; thus, no trend line has been drawn.

Calculation of concentration of acidic and basic sites. The concentration of acid and basic sites on the catalysts (expressed as meq/g) was calculated from the regression data of the linear curves illustrated in Figures 2 and 3. The results are shown in Table 2. Grouping the results according to the number of endpoints found in

**Table 2** Relative concentrations of acidic and basic sites of catalysts, as determined by thermometric titration

Catalyst	Acidic sites, meq/g catalyst		Basic sites, meq/g catalyst		
	Endpoint 1	Endpoint 2	Endpoint 1	Endpoint 2	Endpoint 3
A	0.16		0.97		
B	0.05	0.92	1.20		
C	3.95	0.92	1.40	1.68	1.23

the titration was done as a matter of convenience in presenting the data clearly, and does not imply that the chemical nature of the acidic and basic sites is the same for all catalysts with the same endpoint number.

Series 2: Comparison of catalytic activity as determined by TGA estimation of ammonia absorption and calorimetric analysis. Figure 4 illustrates a linear correlation of results of catalyst activity obtained by the manufacturer using ammonia absorption as determined by TGA, and calorimetric analysis from the heat of reaction with n-BA and the acidic sites on the catalyst.

Series 3: Comparison of thermometric titration techniques with ammonia absorption techniques as measures of catalyst activity and acid site strength. The results of these experiments are presented in a series of graphical plots, in which results of one procedure are plotted against those of another.

Figure 5 shows that the results of the two ammonia sorption techniques are correlated. Figure 6 shows that the results of the ammonia-TPD technique are correlated with the two thermometric titration techniques. Figure 7 shows that the results of the two thermometric titration techniques are correlated.

The coefficients of correlation ( $R^2$ ) for the regression lines illustrated in Figures 5, 6, and 7 were calculated, and are listed in Table 3.

## Discussion

### Interpretation of titration thermogram

It has been suggested by Pratt<sup>8</sup> that the second derivative curve can give a qualitative view of the breadth and modality of the distribution of the acidic sites. This is seen in Figure 1, where three distinct endpoints and one probable endpoint (a shoulder preceding the first endpoint) suggest that there are at least three and possibly four types of acidic sites, grouped by virtue of similar binding energies. Table 1 presents data showing that the temperature rise as a function of titrant addition is higher for the shoulder and the first endpoint than for the second and third endpoints. This observation is consistent with a hypothesis that the shoulder and the first endpoint represent a quantitation of Brønsted (proton donor) acidic sites, since it would be anticipated that the relative enthalpy change would be higher in cases of Brønsted acidity compared to Lewis (electron acceptor) acidity. However, in order to obtain quantitative distributions, the enthalpy of reaction must be calculated in each instance.

Series 1: Effect of sample mass on titration of acidic and basic sites. In some cases, more than one endpoint was observed, suggesting that acidic and basic sites on the surface of the catalysts may be categorized on the basis of their relative strengths. It is likely that the strength of active sites is related to

their chemical environment. The term “chemical environment” is used to describe the relative effect of neighboring ions on each other in the crystal lattice. In the case of active alumina catalysts, activity is related to the defect structure of the transition (partially dehydroxylated) forms.<sup>9</sup> A strong linear correlation exists between the mass of sample used and the titers of n-BA or TFA, suggesting that reactions with surface acidic and basic sites are stoichiometric. While the acidic and basic site densities may be quantified from a single measurement, the use of linear regression in this instance probably increased the reliability of the estimation. The rapidity of the thermometric titration permits a considerable amount of valuable data to be gathered in a very short time. The simplicity of the procedure means it can be employed for routine process and product quality control.

Series 2: Comparison of catalytic activity as determined by TGA estimation of  $\text{NH}_3$  absorption and calorimetric analysis by reaction with n-BA. Figure 5 illustrates that a simple experiment to measure the temperature effects of the heat of reaction between n-BA and surface acidic sites gives results that correlate well with an industry-recognized procedure ( $\text{NH}_3$  absorption, as determined by TGA). Compared to the exacting and tedious TGA procedure, which requires complex and expensive equipment, the calorimetric procedure may be performed in a minute or so. Because heat of reaction may be correlated with strength of acidic or basic sites, it is a useful tool for evaluating overall catalyst activity.

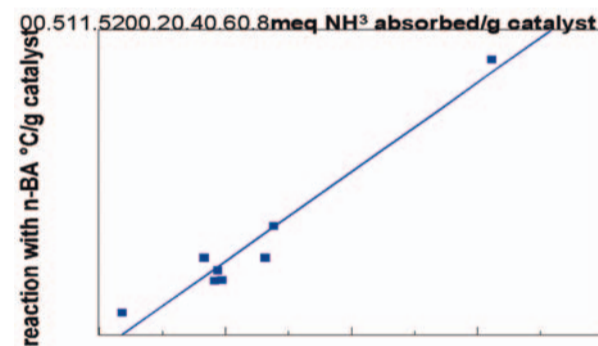


Figure 4 Comparison of catalytic activity as determined by TGA estimation of  $\text{NH}_3$  absorption and calorimetric analysis by reaction with n-BA.

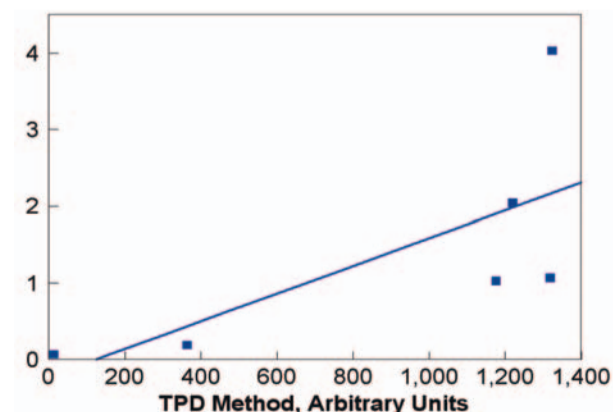


Figure 5 Correlation of results of TPD and TGA ammonia absorption analysis methods.

Where definite endpoints may be identified, a titration procedure can yield valuable information concerning acidic and basic site densities. Where multiple endpoints are analyzed, this may indicate that such sites may exist in groupings according to their chemical environment. Calorimetric data can yield information concerning the relative strengths of these active sites.

Series 3: Comparison of catalytic activities of zeolitic catalysts as determined by ammonia sorption and thermometric titration methods. The ammonia TPD and TGA methods have been used extensively for the determination of the acid sites and strengths of catalysts and their supports. In the data presented here (Figure 5 and Table 3), results of the two methods correlate poorly, although it was noted that samples presented for TGA analysis were subjected to different pretreatments.

The TPD results correlated well with the thermometric titration results, and correlation of the two thermometric titration methods was very good, suggesting an excellent level of self-consistency between the methods.

Continuous titration at constant rate has been carried out previously on zeolites.<sup>10,11</sup> Punctuated titration has been proposed<sup>8</sup> to take into account relatively slow diffusion of titrant into the micropores of the catalyst. The difference in the results between the two thermometric titration methods suggests that a significant proportion of acid site catalytic activity in the zeolite samples analyzed is diffusion controlled.

It is feasible to conduct fully automated continuous and punctuated thermometric titrations, which take only a few minutes each to perform. In comparison, the ammonia TPD method takes nearly 4 hr per sample.

## Conclusion

Automated thermometric titrimetry may reveal much useful information about the activity of catalysts. Acidic or basic site density may be determined by titration, respectively, with an appropriate base or acid in nonaqueous media. Activity strength may also be simply estimated by reaction with a fixed amount of acid or base, and by observing the temperature increase as a function of sample mass. Comparison of titrations conducted at a constant rate with those performed with punctuated addition of titrant can reveal the extent to which activity is diffusion controlled. Such thermoanalytical techniques, which may be undertaken with an automated thermotitrator, are simple and robust, and can yield much useful information in a very short time. They can complement or even supplant established techniques, and are well-suited for process and quality control laboratories.

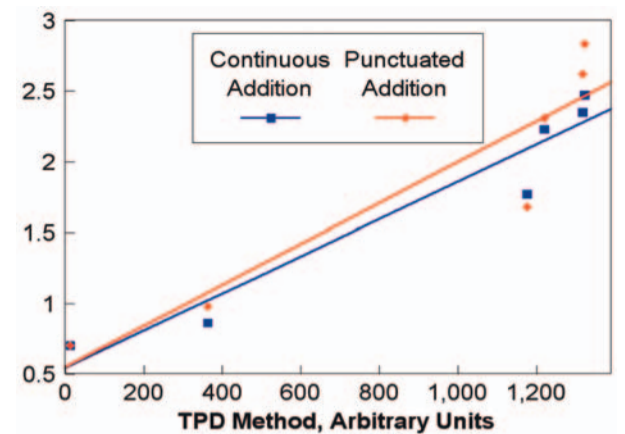


Figure 6 Correlation of results by TPD ammonia absorption and thermometric titration methods.

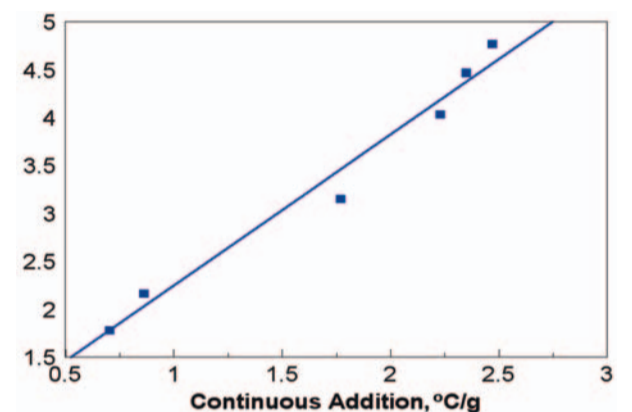


Figure 7 Correlation of results by continuous addition and punctuated addition thermometric titration methods.

**Table 3** Correlation of various methods used to estimate acid site strength of catalysts

Method correlation	Coefficient of correlation ( $R^2$ )
TPD vs TGA (ammonia sorption methods)	0.49
TPD vs continuous addition thermometric titration	0.93
TPD vs punctuated addition thermometric titration	0.87
Continuous vs punctuated thermometric titrations	0.98

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