TA Instruments

Thermal Analysis & Rheology

Thermal Analysis Applications Brief

TGA Evaluation of Zeolite Catalysts

Number TA-231

SUMMARY

The relative strength and distribution of acid sites in a zeolite is an important indicator of its catalytic properties. One method to accurately measure the acidity of zeolites is to study the temperature programmed desorption (TPD) of a base from the zeolite surface (1). Thermogravimetric analysis (TGA) is a useful tool for characterizing the TPD profiles of zeolites.

INTRODUCTION

Zeolites are porous materials whose structures are based on a crystalline network of SiO_4 and AlO_4 tetrahedrally linked together by common oxygen atoms (2). The zeolite framework contains channels and interconnected voids which, when first crystallized, are occupied by water and cations. The cations are required to balance the net negative charge on the zeolite framework created by the presence of the Al^{3+} ions surrounded by the four shared oxygen atoms.

When the charge-balancing cations are exchanged into H^+ cations, zeolites become particularly useful as catalysts. The abundance and relative strength of these acid sites are good indicators of the catalytic properties of a zeolite. Therefore there is a need to quickly and accurately measure the acidic properties of new zeolites as they are synthesized in order to evaluate their catalytic potential.

By exposing an acidic zeolite to a base (e.g. ammonia, isopropylamine, etc.), the acid sites become neutralized. Basic molecules have higher affinity for strong sites than for weak sites, thus the basic molecules can be desorbed from weak sites at lower temperatures than are required to desorb them from stronger sites. This is the underlying theory of TPD. TGA can be used to accurately detect the desorption of basic molecules from a zeolite as a function of temperature and the resulting data can be used to calculate the acid site strength and distribution of various zeolites.

EXPERIMENTAL

TGA-TPD studies were conducted on the same set of zeolites located in two different laboratories using TA Instruments Thermogravimetric Analyzers (TGA 951 and TGA 2050). The experiments using isopropylamine were performed in one laboratory using a TGA 951 and the experiments using ammonia were performed in another laboratory using a TGA 2050. Different bases and instruments were chosen to illustrate the adaptability of the method.

Ammonia and isopropylamine were selected for several reasons. Ammonia desorption was chosen since it is specified in a pending ASTM standard test method ["Determination of Zeolite Acidity and Acid Strength Distribution by Temperature Programmed Ammonia Desorption (TPD)"] under consideration of ASTM Subcommittee D32.01 on Physical-Chemical Properties of Catalysts. The procedure described herein closely resembles an early draft of this ASTM method. Isopropylamine was chosen as a second base to study based on earlier results described by Pereira and Gorte (3).

PRECAUTIONS

Care must be taken when using corrosive gases in your TGA. If used improperly, some gases may cause personal injury or damage to your instrumentation. Always check the MSDS for any base that you intend to use to be aware of important safety and hazard information and follow the guidelines outlined below:

- Work in a well-ventilated area with gases such as ammonia and isopropylamine in case there are small leaks present in your gas plumbing. Ideally, the TGA should be placed in a fume hood to minimize exposure risks in the event of a leak. If this arrangement is not feasible, be sure to attach a tube to the outlet of the TGA furnace to carry the exhaust to a fume hood and take care to ensure tight gas connections to the TGA.

- Protect your TGA balance assembly by always ensuring that at least 10% of your total gas flow is composed of pure helium (or another inert gas) and that only 100% inert gas is routed through the balance chamber. Failure to provide an inert purge through the balance chamber will result in back-diffusion of your furnace purge gas into the balance chamber which may result in damage to the delicate balance assembly.

- Additional precautions when using isopropylamine: in addition to being flammable and toxic, isopropylamine is incompatible with most types of flexible tubing. Standard tygon tubing is noticeably degraded by isopropylamine vapors in only one day. Teflon tubing with compression fittings (e.g., Swagelok®) is recommended for use with isopropylamine. When the compatibility of a specific tubing with a specific base is in doubt, check chemical compatibility tables.

- The presence of moisture in the purge gas may affect the results. It is important to ensure that the purge gas is dry and that all gas connections are leak-free. To ensure that the purge gas is dry, it is wise to pass it through a drying agent. The choice of drying agent is limited since the chosen drying agent must adsorb water better than the zeolite studied (this eliminates molecular sieves) and it also must not adsorb ammonia or the base which is used. One possible choice is BaO, however, BaO is toxic. Please consult the MSDS before using BaO as a drying agent.

REAGENTS

For the experiments outlined in this applications brief, a mixture of 5% ammonia in helium was used. Ammonia gas mixtures are available from most cylinder gas suppliers as a special order item. Some other bases (such as isopropylamine) are liquids at room temperature. In order to introduce these bases into the TGA as a gas, it is necessary to bubble helium (or another inert gas) through the base and then pass the resulting vapor into the TGA furnace. With this arrangement, care must be taken to ensure that the vapor does not condense in the gas tubing and possibly enter the TGA as a liquid. Appropriate liquid traps should be set up before the TGA to catch any condensed liquids. You may wish to consider other ways to prevent condensation in the gas tubing such as heating the gas purge tubing and/or diluting the vapor with inert gas.

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SUMMARY OF METHOD

A TPD experiment can be divided into four steps as outlined below:

STEP 1 - PRETREATMENT

The sample must be preheated to remove adsorbed water and other volatiles. Heat the zeolite sample in a flowing helium atmosphere (both in the balance and furnace ports) to 500°C. A 10°C/min heating rate is typically used but the actual rate is not important. Hold isothermally at 500°C until a constant mass is achieved (approximately 5 to 10 min). [Note: 500°C should be suitable for most samples. Depending on the nature of the sample, lower or higher temperatures may be used.]

Once a constant mass is achieved, program the furnace to cool to 100°C. The mass should remain constant as the sample is cooled. If an increase in mass is observed then there is likely a leak in one of the purge lines allowing moisture to enter the system.

STEP 2 - ADSORPTION OF BASE

When the sample has equilibrated at the specified temperature (e.g., 100°C), the furnace purge is switched from the inert gas to the gas containing the base. [This can be accomplished automatically using a TA Instruments Gas Switching Accessory (GSA).] A weight gain is observed as the base is adsorbed. After approximately 10 minutes the sample should reach a constant mass. (IMPORTANT: Ensure that a flow of inert gas is maintained through the balance chamber throughout the duration of the experiment.)

STEP 3 - DESORPTION OF PHYSISORBED BASE

Once the sample has adsorbed all of the base that it can at 100°C, the furnace purge should be switched back to an inert atmosphere. As a result, the sample will begin to lose mass as basic molecules that were physisorbed to the surface begin to desorb. This desorption of the physisorbed base molecules should be allowed to continue at 100°C for about one hour or until the mass is nearly constant.

STEP 4 - TEMPERATURE PROGRAMMED DESORPTION

After desorption of the physisorbed base molecules is complete, the temperature is increased to remove the remaining base molecules. Typically, a heating rate of 10°C/min to a maximum temperature of 600°C is used. At least two weight loss regions are observed for acidic zeolites. The initial mass loss can be attributed to desorption from weakly acid sites and the mass loss that begins at higher temperatures (~250 °C) can be attributed to desorption from strongly acidic sites.

RESULTS

The various steps of a TGA-TPD experiment are shown in Figure 1 for an HZSM-5 zeolite sample conducted using an ammonia base. Note that sample size used in calculation is the sample mass after pretreatment. This is done so that 100% represents the sample mass after pretreatment. This is required for proper acidity calculations.

A close-up of the chemidesorption portion of the experiment (step 4) is shown in Figure 2. Two weight loss regions are observed corresponding to the desorption of weakly bound ammonia molecules associated with weak acid sites and the desorption of strongly bound ammonia molecules associated with strongly acidic sites respectively. The peak minimum of the TGA derivative curve identifies the temperature at which desorption from weakly acidic sites stops and desorption from strongly acidic sites begins. From this data it is possible to quantitatively identify the number of strong and weak acid sites present in the sample being investigated.

The acidity of a zeolite is calculated by the following formula and reported in units of millimoles of acid sites per gram of zeolite.

$$Acidity = \frac{W(g) \text{ x} \left(\frac{1}{\text{MW of Base}}\right)\left(\frac{1000mg}{1g}\right)}{\text{Mass of zeolite after pretreatment (g)}}$$

where *W(g)* is the mass loss due to the desorption of base in the temperature range of interest.

Since W(g) divided by the mass of the zeolite after pretreatment is simply a percentage mass loss, therefore equation can be simplified by just reading the % Mass Loss from the desorption curve.

$$Acidity = \left(\frac{\text{\% Mass Loss}}{100}\right)\left(\frac{1}{\text{MW of Base}}\right)\left(\frac{1000mg}{1g}\right)$$

For the sample pictured in Figure 2, the acidity calculations are shown below:

$$Weak = \left(\frac{0.5848}{100}\right)\left(\frac{1mmol}{17mg\ \text{NH}_3}\right)\left(\frac{1000mg}{1g}\right)$$

$$Weak = 0.34\ mmol\ /\ g$$

$$Strong = \left(\frac{0.5373}{100}\right)\left(\frac{1mmol}{17mg\ \text{NH}_3}\right)\left(\frac{1000mg}{1g}\right)$$

$$Strong = 0.32\ mmol\ /\ g$$

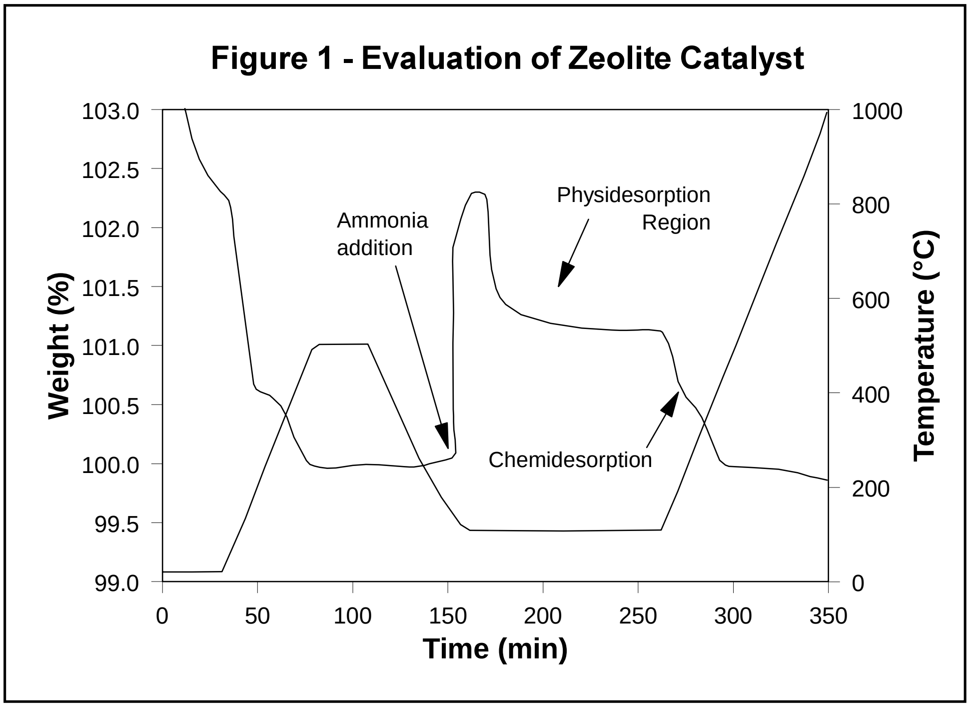


Figure 2. Chemidesorption Region

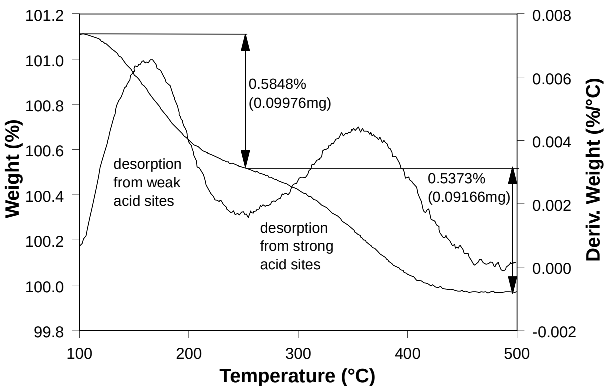


Figure 3 shows the TGA derivative curves for the chemidesorption region for samples with different $SiO_2/A1_2O_3$ ratios using ammonia, and Figure 4 shows similar data for experiments performed using isopropylamine. Table 1 shows the calculated weak and strong acidity values for the data in Figures 3 and 4. Note that the acidity increases with decreasing $SiO_2/A1_2O_3$ ratios (SAR). The increased acidity is the result of the inclusion of more aluminum atoms in the zeolite framework. Isopropylamine has a higher molecular weight (59 g/mol) than amonia. As a result, the samples run with isopropylamine are more sensitive to desorption (e.g., greater weight loss).

		Acid Site Density (mmol/g)			
Sample ID	$SiO_2/A1_2O_3$ Ratio	Investigator A (Isopropylamine)		Investigator B (Ammonia)	
		weak	strong	weak	strong
5020E	55	0.5	0.38	0.34	0.32
8020	82	0.38	0.26	0.36	0.21
1502	133	0.22	0.15	0.12	0.1

Figure 3. Zeolite Comparison - Ammonia

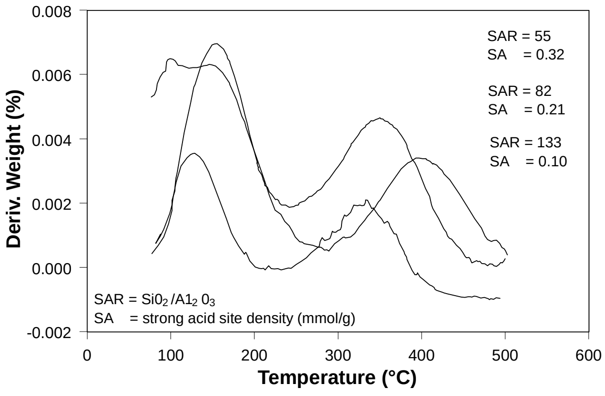
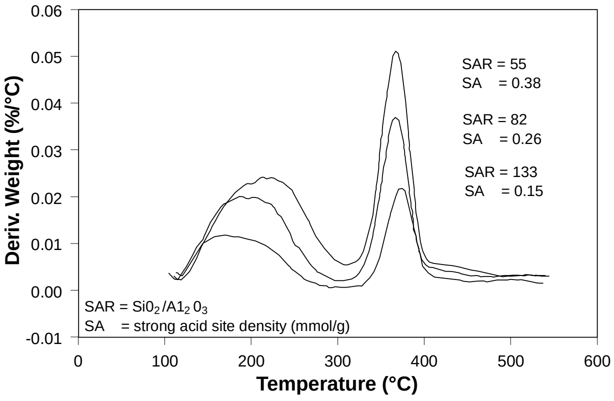
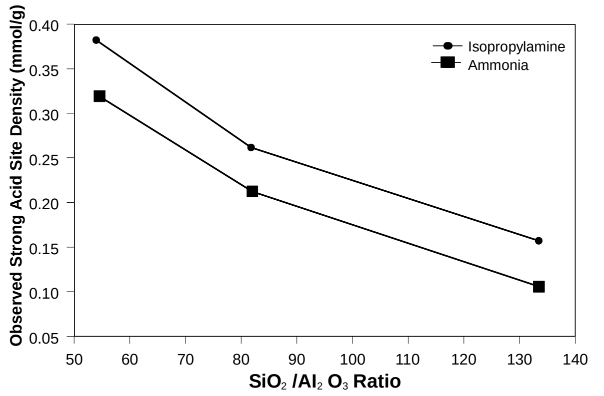


Figure 4. Zeolite Comparison - Isopropylamine



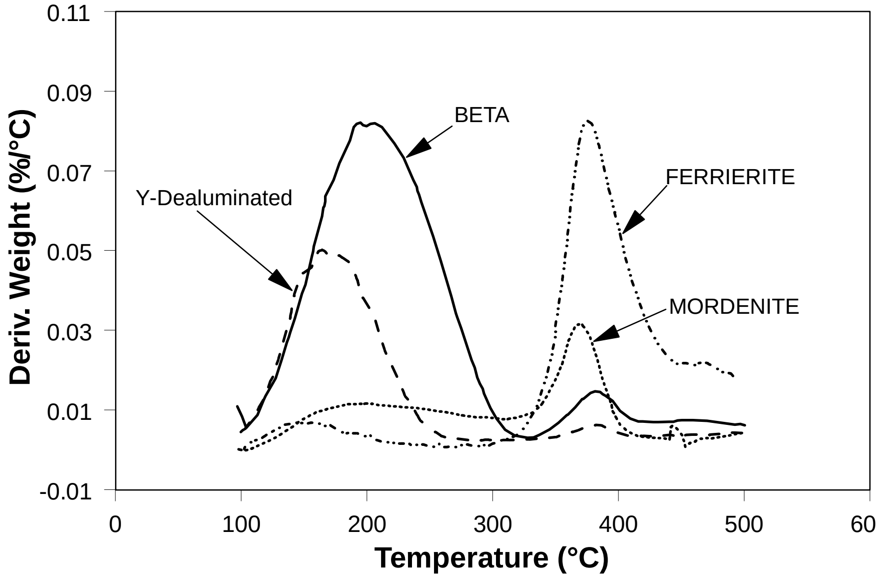
Zeolites are most often characterized by their strong acid site density. The strong acid site density is used as an indicator because the weak acid site density is more influenced by other factors such as base used, and time and temperature of physidesorption. Figure 5 illustrates the relationship between acid site density and $A1_3+$ content, and demonstrates good correlation between the isopropylamine and ammonia experiments.

Figure 5. Observed Strong Acid Site Density as a Function of $Si0_2/A1_20_3$ Ratio



The utility of this method in differentiating zeolites was demonstrated by studying several other samples. Members of the Beta, Mordenite, Ferrierite, and zeolite Y families were studied using isopropylamine as the base. The results are shown in Figure 6. It is shown that different zeolite families can have different acid strengths and distributions. Peak shape and intensity may differ depending on many factors including the SiO_2/Al_2O_3 ratio, the cation content, or a number of other characteristics.

Figure 6. Zeolite Comparison - Different Acid Strengths



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