A tool for predicting the integrity of Y zeolite crystalline structure

Differential thermal analysis

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Abstract The purpose of this work was to employ the differential thermal analysis technique (DTA) to compare variations in the collapse energy of the Y zeolite crystalline structure in a fresh sample and in the sample after temperature treatment and impregnated with 3,000 ppm of vanadium and nickel. A small exothermic signal in the DTA curve at 950–1,150 °C indicated the collapse of the crystalline structure. The areas of the exothermic signals in the DTA curves of the samples indicated a 20% reduction in the exothermic area peak of sample treated 600 °C for 3 h and 25% reduction in same peak in the metal impregnated Y zeolite. These results were compared with X-ray data leading to the conclusion that metal impregnation affects the Y zeolite crystalline structure and that the DTA technique is a potentially useful tool for measuring the integrity of Y zeolite in catalysts.

Keywords Y zeolite · Structure collapse · Thermogravimetry

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Introduction

A fluid catalytic cracking (FCC) catalyst is a porous microsphere containing Y zeolite dispersed in a clay matrix (kaolin and alumina). Y zeolite is the rate-controlling constituent during the catalyst cracking process [1] and the matrix performs both physical and catalytic functions. Hence, its stability is crucial to the rigors of the cracking process. Heavy metals existing in petroleum feedstock, such as vanadium and nickel, have the most significant impact on the performance of FCC catalysts [2–4]. During the cracking process, these metals are deposited in the catalyst and affect both catalyst and selectivity. Vanadium species have mobility, mainly in the presence of steam, and can migrate onto the surface of zeolite to destroy its structure [4–7].

Extensive research on zeolitic FCC has focused on understanding the destructive role of vanadium, since it is a major issue for catalyst performance during the cracking of residuum-containing feeds [3, 4, 8].

Differential thermal analysis (DTA) is a thermal analysis technique that measures the difference in temperature between the sample and a reference material while they are both subjected to the same heating process [9]. DTA has been employed to evaluate catalysts, providing valuable information about changes in heat, the specific surface area determined by N_2 adsorption–desorption and to screen activity of different catalysts [10–12].

However, DTA has not been successful in providing a general, reproducible and standard method for measuring and recording thermal stability. Many factors affect the temperature at which the event is observed. Therefore, it is useful for direct comparisons, i.e., to obtain data using the same device and under the same conditions [9].

The purpose of this work was to employ the differential thermal analysis technique (DTA) to compare variations in

the collapse energy of the Y zeolite crystalline structure before and after thermal treatment and the influence of vanadium and nickel. The collapse energy is measured by DTA and the result compared with X-ray powder diffraction.

Experimental

Samples

A sample of fresh Y zeolite was selected for this study. The same sample was impregnated with vanadium and nickel by traditional impregnation methodology [13]. Before metal impregnation, Y zeolite is activated at 540 °C and after impregnation with organometallic compounds it is calcined at 600 °C for 3 h. Thereafter the sample of fresh Y zeolite was treated at 600 °C for 3 h to observe the temperature action in its structure.

Thermogravimetry and differential thermal analysis

All the experiments were conducted in a Netzsch STA-Luxx 409 thermal analyzer, using alumina crucibles (300 μL) at a heating rate of 50 K min^{-1} and an initial sample mass of 80 mg in a dynamic atmosphere of N_2 at 100 mL min^{-1} from 35 to 1,200 °C. The sample's temperature was measured with a thermocouple attached directly to the crucible, i.e., very close to the sample. Temperature and signal calibrations were performed with $RbNO_3$, $KClO_4$ and $CsCl$.

The STA-Luxx 409 simultaneous thermal analyzer allows recording thermogravimetric and differential thermal analysis (TG/DTA) signals at the same time. Its use therefore enabled us to monitor the mass loss of the catalyst during heating. The calculation of the area of the exothermic event in DTA curves is expressed in energy units per gram of sample (J/g). The release energy was calculated based on the mass at the beginning of the exothermic event. This calculation was made possible by the simultaneous TG/DTA analyzer.

The analyzer software allows one to calculate the first derivative curve of mass loss (DTG), which is useful information about the initial and final temperature of each event. To facilitate viewing, we used the resources of a data handling program which allows the DTA curve to be adjusted so that it starts at 0 mW/mg.

X-ray diffraction

The X-ray diffraction patterns were recorded on a BRUCKER D8 diffractometer using Cu Kα radiation from 3° to 70° at step of 0.5° and 3° s/step.

The samples crystallinity was calculated based on ASTM3906 methodology [14]. The fresh Y zeolite was considered as a reference sample (100% crystalline). XRD

diffractograms of all samples are obtained under the same conditions as describe.

The samples' X-ray diffraction intensities of the (533) peak (23.5°) are compared to provide % XRD intensity/reference Y zeolite(533). The intensity ratio, expressed a percentage of crystallinity:

$$\frac{\text{XRD Intensity}}{\text{NaY(533)}} = 100 \times \frac{C_x}{C_R}$$

where:

NaY   reference sample that is Y zeolite
C_x height of the peak peak for the sample and,
C_R height of the peak peak Reference NaY

Controlled furnace

A controlled furnace was used to heat the samples first at 540 °C for 3 h and after at 600 °C for 6 h.

Vanadium and nickel impregnation

The samples containing vanadium and nickel were prepared following the method described by Mitchell [13]: a suitable amount of V and Ni organometallic compounds was added to samples in two manners: separately or at same time. The mixture was grounded thoroughly and heated at each component was heat 540 °C in controlled furnace for 3 h and calcined at 600 °C for 6 h. The amount of vanadium was chosen based on the traditional cyclic impregnation and aging treatment for activity studies.

Results and discussion

In a preliminary experiment each Y zeolite, was analyzed by TG/DTA in a nitrogen atmosphere, applying a heating rate of 50 K min^{-1} to observe the thermal behavior with respect to mass and energy variations resulting from the different events that the samples underwent.

The resulting TG curve (Fig. 1) indicated that fresh Y zeolite sample showed two different events. The first loss was caused by the evolution of bound water (120–400 °C) and the second, a little one with loss mass of 0.5% occurs during the collapse of crystalline structure (950–1,100 °C).

The DTA curve showed endothermic event involved in energy related water release, as previously mentioned (Fig. 2a). A second one presented an exothermic event at 950–1,150 °C which is clearly visible in the magnified curve in the region of 950–1,200 °C (Fig. 2b). This event represents the collapse of the Y zeolite structure [15, 16]. The release energy was calculated by the peak area determination based on the mass at the beginning of the exothermic event. The Y zeolite collapse energy is about 152 J/g.
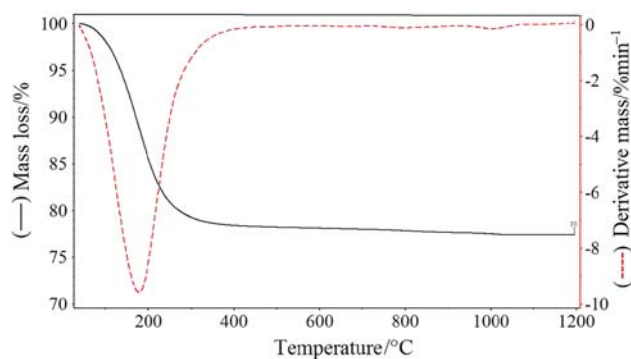
Fig. 1 TG and DTG curves of Y-zeolite samples at 50 K min^{-1} in N$_2$ flow (50 mL min^{-1})
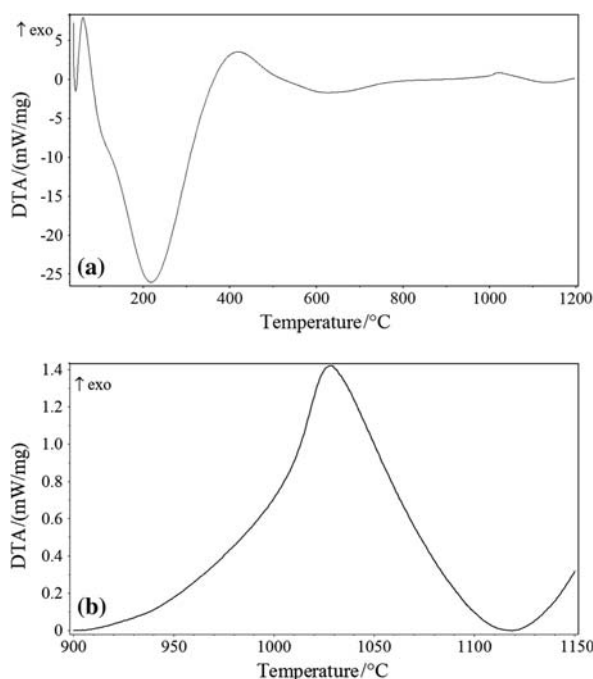

Fig. 2 DTA curve of **a** Y zeolite sample and **b** DTA curve of Y zeolite amplified between 900 and 1,150 °C

During FCC process, the catalyst is submitted on high temperatures and during the cracking process metals are deposited in it affecting both, catalysis and selectivity. Therefore, to study the influence of temperature, the Y zeolite was heated in controlled furnace at 540 °C for 3 h to water release and at 600 °C for 6 h. After that they were analyzed by XRD and TG/DTA to quantify the collapse energy. To study the influence of metals on the Y zeolite crystalline structure, it was impregnated with 3,000 ppm of vanadium, 3,000 ppm of nickel and a mixture of 3,000 of nickel and vanadium as explained in experimental part. After the metal impregnation, the samples were analyzed by TG/DTA (Fig. 3).
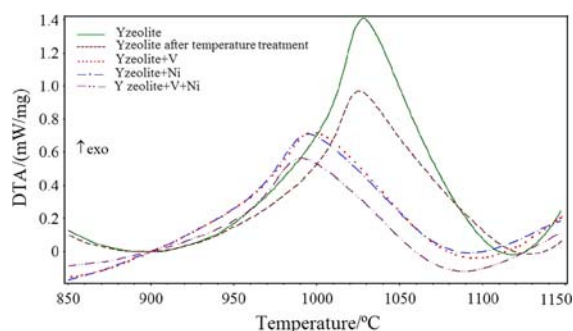

Fig. 3 DTA curves amplified between 850 and 1,150 °C of: Y zeolite, Y zeolite after temperature treatment, Y zeolite + V, Y zeolite + Ni and Y zeolite V + Ni

Table 1 Exothermic peak area (J/g) from Y zeolites DTA curves

| Test | Exothermic peak from DTA/J g^{-1} | | | | |
	Y zeolite	Y zeolite Temp. treatment	Y zeolite + V	Y zeolite + Ni	Y zeolite + V + Ni
1	150	122	112	112	102
2	148	121	117	113	99
3	152	128	107	114	104
4	150	122	118	114	111
5	158		117	113	
6	151		116	115	
Medium	152	123	114	113	104
SD	3.15	2.77	3.86	0.96	4.42

SD standard deviation

The DTA curves showed different areas for exothermic signals of the samples. The fresh Y zeolite presented larger area than those other treated samples. The peak area decreases by 20% after temperature treatment and about 30% after metal impregnation (Table 1). Apparently vanadium, nickel and the mixture of them cause the same effect in zeolite structure.

The reproducibility of the results was verified through replications of Y zeolites samples tested under the same TG/DTA conditions. Table 1 describes the area of the exothermic signals found in the amplified DTA curves and the average values compared statistically by Student's *t*-test [17]. It indicates that only the impregnated samples present the same values, which are different for the samples without metals.

The resulting diffractograms showed a pattern of crystalline structure for all Y zeolite samples, with sharp and well-defined peaks (Fig. 4), indicating that they still retained a certain state of crystallinity after temperature and impregnation with metal. But assuming that the fresh Y zeolite has 100% of crystallinity one can observed that the other samples have their cristallinity affected after
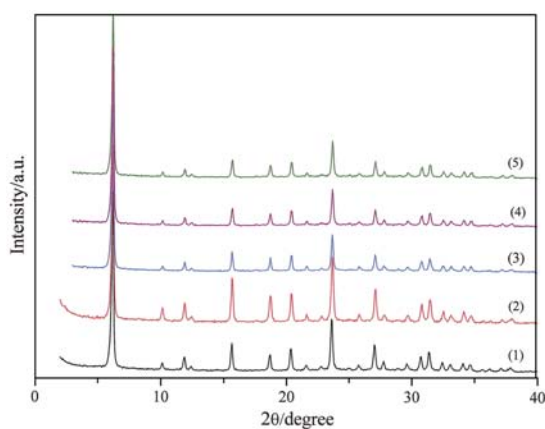
Fig. 4 XRD of Y zeolite samples: (1) Y zeolite, (2) Y zeolite after temperature treatment, (3) Y zeolite + Ni, (4) Y zeolite + V and (5) Y zeolite + V + Ni

Table 2 DTA and XRD results

Sample	Exothermic peak from DTA/J g^{-1}	XRD crystallinity/%
Fresh Y zeolite	152	100
Y zeolite after temperature treatment	123	86
Y zeolite + V	114	60
Y zeolite + Ni	113	59
Y zeolite + V + Ni	100	54

treatments (Table 2). The crystallinity decrease 14% after temperature action and about 40% after metal impregnation.

These differences may have resulted from the introduction of the metal, which would not be surprising since it is well known that vanadium, per se, has little effect on Y zeolite stability [2].

Comparing the XRD and DTA results (Table 2) one can conclude that the sensitivity of DTA technique is enough to quantify the crystalline modifications in Y zeolite caused by temperature and metal impregnation. Vanadium species have mobility, mainly in the presence of steam and can migrate onto the surface of zeolite to destroy its structure [3]. The steam was not introduced in present study although to be the principal responsible to destroy the zeolite crystalline structure, however, the important thing is that even without the presence of steam, DTA observed changes in the Y zeolite collapse structure after metal introduction.

Conclusions

DTA technique proved sufficiently sensitive to detect slight changes in the integrity of three-dimensional structures of Y zeolite. The DTA technique did not provide reproducible results for thermal stability measurements, but proved quite good for straightforward comparisons. The results presented here indicate the relevance of conducting more in-depth studies to correlate the collapse energy of the Y zeolite in a specific catalyst with its resistance to high vanadium concentrations. Our studies continue, seeking to correlate the area of the exothermic signal obtained by the DTA curve and catalyst stability results obtained by traditional methods.

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