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Brønsted acid site number evaluation using isopropylamine decomposition on Y-zeolite contaminated with vanadium in a simultaneous DSC–TGA analyzer

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Abstract

Acid-site catalyzed decomposition of isopropylamine was followed in a simultaneous DSC–TGA analyzer. USY zeolite samples with and without vanadium were studied. Results show that acid sites number decreases linearly with vanadium concentration in zeolite indicating that vanadium neutralizes acid sites on catalyst and the metal is able to move on the surface of the solid. The neutralizing species probably contain only one vanadium atom. The reaction enthalpy plus desorption heat of the products show that vanadium preferentially neutralizes the strongest acid sites on the zeolite. The application of the simultaneous DSC–TGA technique to quantify Brønsted acid sites on solids by this reaction is novel.

Keywords: Y-zeolite; Vanadium; Isopropylamine decomposition; Acid sites quantification

1. Introduction

Fluid catalytic cracking (FCC) is the most widely used process for conversion of the heavy fraction of crude oil into gasoline and other valuable hydrocarbons in oil refineries. The Y-zeolite is the main active component of FCC catalysts because of its acid characteristics and temperature stability [1]. The FCC process is very important in the production of gasoline and other petrochemical products [2]. Petroleum has metal contaminants such as vanadium, sodium and nickel that affect catalyst performance and influence the operation of FCC units in different ways [1–6]. It has been shown that vanadium disables the catalyst [7], destroying the zeolite [5–7]. To explain the action of vanadium on Y-zeolite several mechanisms have been proposed [5–9], nevertheless, the more recent proposals involve the combined sodium–vanadium action and sharing the neutralization of Brønsted acid sites of zeolite by vanadium species [7–9]. The neutralization of acid sites by vanadium species was proposed by Torrealba et al. [10] and used by Trujillo et al. [7] to explain the destruction of the zeolite, however, there is no experimental evidence that supports this in the literature.

The reaction of catalytic decomposition of isopropylamine (*i*-Pam) in propylene and ammonia has shown to be a useful tool for the quantification of acid sites in acid solids [11–18], Adsorption complexes with 1:1 stoichiometry of 2-propanamine (*i*-Pam) over Brønsted acid sites of ZSM-5 was observed by first time by Kofke et al. [11]. The same authors using temperature-programmed desorption (TPD) technique provided with a mass spectrometer detector showed that adsorbed amine decomposes on ammonia and propene following a Hofmann elimination at temperatures between 575 and 650 K. It appears that reaction occurs so long as the sites are able to retain the alkylammonium ion up to its characteristic decomposition temperature without desorption by reverse proton transfer. The chief advantage of the use of *i*-Pam as a probe for heterogeneous acid-site densities is that the temperature-programmed decomposition

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Table 1
Vanadium concentrations on Y-zeolite samples

Zeolite	Concentration (mmol V/g zeolite)
Z-0	0.000
Z-V2	0.018
Z-V3	0.027
Z-V5	0.054
Z-V10	0.105
Z-V12	0.123
Z-V15	0.159
Z-V18	0.180

reaction occurs only at Brønsted sites, not Lewis sites [12]. Amine molecules adsorbed in excess of one/Brønsted acid site desorb unreacted at lower temperatures and based on the observation that the decomposition temperature for isopropylamine is identical on H-[GalZSM-5 and H-[FelZSM-5, the reaction temperature does not appear to depend on the composition of the lattice [12]. Products are the same if the reaction is carried out in vacuum or inert gas [14]. The sites responsible for reaction of isopropylamine in TPD also appear to be responsible for hydrocarbon cracking [19,20] on steamed H–Y catalyst and amorphous silica–aluminas [21].

The reaction has been followed mainly with experimental arrangements that involve mass spectrometers able to determine the products from the reaction as a function of temperature. In this work, studies took place in a simultaneous analyzer differential scanning calorimeter (DSC) and thermogravimetric analyzer (TGA) that allowed us to simultaneously measure *i*-Pam mass decomposed in the catalysts and the energy involved in the reaction as a way to quantify the number of acid sites and characterize its strength.

2. Experimental

The study was made on a USY zeolite, reference CVB712, from Zeolyst International. The supplier reports the following typical properties: SiO_2/Al_2O_3 molar ratio: 12, unit cell size: 24.35 Å, surface area measured at P/P_0 0.03: 730 m^2/g.

Metal impregnation procedure used is similar to that described by Mitchell [22] using vanadium naphtenate and toluene as solvent.

The size of vanadium containing molecules and the presence of water inside the zeolite guarantees that the metal be deposited on the external surface of the zeolite. The impregnated product was calcined first at 573 K for 5 h in a muffle oven supplied with dry air flow to eliminate organic material. Precalcined zeolite was calcined for 16 h in a vertical quartz tube with synthetic dry air flow at 1033 K. In both thermal procedures a heating rate of 2 K min^{-1} was used. Before the analysis calcined samples were allowed to sorb water in a room with 50% relative humidity controlled atmosphere. Table 1 shows vanadium concentrations on zeolite and nomenclature of the samples.

A simultaneous DSC–TGA analyzer model STA-625 from Rheometrics Scientific, calibrated against melting points and fusion enthalpies of indium and lead was used for this research. The sample (3.00–3.60 mg) in aluminum cups was first flushed in a dried air flow at a rate of 40 N mL min^{-1} while heated to 423 K at a rate of 10 K min^{-1}, subsequently the rate was increased at 20 K min^{-1} to reach 823 K were it was kept for half an hour. At the end of this period air was changed for N_2 99.995% (40 N mL min^{-1}) and temperature lowered to 473 K. When the energy flow and mass base line were stable, N_2 flow was switched to pass through a saturator kept at 255 K with a 5-cm column of *i*-Pam. When isopropylamine reaches the sample, adsorption takes place and DSC shows a highly exothermic peak. When the heat flow curve returned to base line (about 5 min) the sample exposure to *i*-Pam was switched off and turned back to pure N_2. Excess *i*-Pam is desorbed and DSC shows an endothermic peak, when the heat flow returned to the base line, temperature was increased at a rate of 5 K min^{-1}. *i*-Pam decomposition occurs in the range of 588–637 K where DSC shows an endothermic peak.

3. Results and discussion

Fig. 1 shows a typical curve obtained in the experiment. The mass curve shows small noise peaks where the valve is changed in position to let *i*-Pam flow in and out of the calorimeter. Adsorption exothermic peak stands out in the DSC curve and then, when amine contact is stopped, the curve shows an endothermic peak of the desorption of physisorbed *i*-Pam. When temperature rises, excess *i*-Pam continues desorbing but in the 589–635 K range an endothermic peak that corresponds to an important change in the mass curve is observed. Other authors have reported that reaction takes place in the range between 575 and 650 K [11–18].

Figs. 2 and 3 show in more detail, and as a function of temperature, the DSC and TGA thermogram of the catalytic decomposition of *i*-Pam on Y-zeolite for the samples without vanadium (Z-0) and with vanadium (Z-V5). It is observed that the endothermic peak and the mass change in the 589–635 K range are less pronounced when the zeolite contains vanadium.

With the TGA analysis data the mass change corresponding to the *i*-Pam decomposition reaction is obtained in the reaction range identified using the DSC curve. The mass change allows the calculation of the number of Brønsted acid sites in

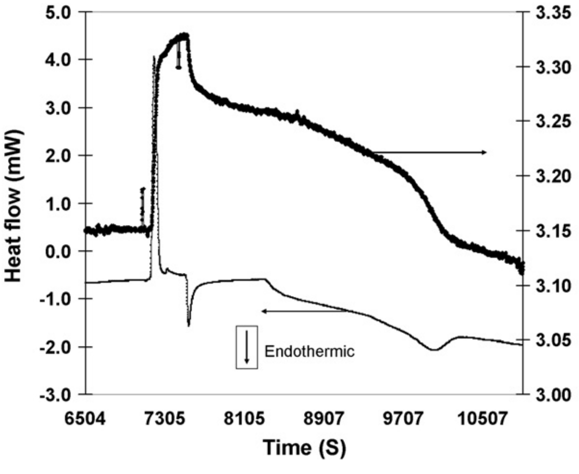

Fig. 1. Typical curves obtained by the DSC–TGA analysis, sample (Z-V3).

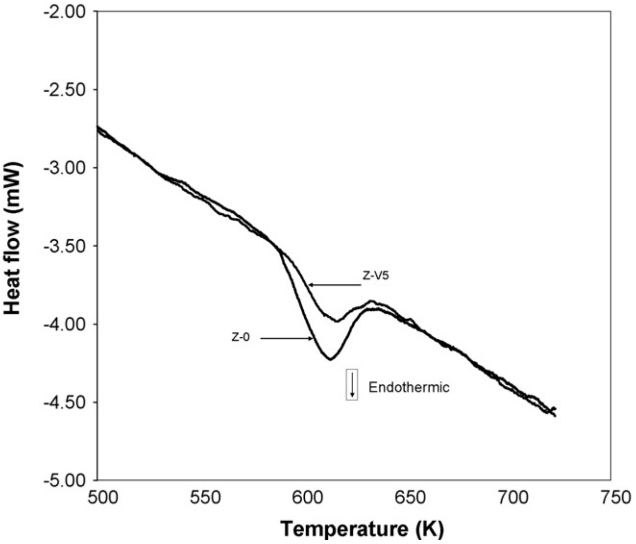

Fig. 2. DSC for the samples without vanadium (Z-0) and with vanadium (Z-V5) normalized to the same mass of the zeolite.

the sample based on one molecule of *i*-Pam/one Brønsted acid site stoichiometry [11]. The DSC curve allows calculating the enthalpy of the reaction plus heat of desorption of products, and as the number of molecules are known from the TGA curve this value can be presented by mol of *i*-Pam. Fig. 4 shows the number of acid sites per gram of zeolite as a function of the amount of impregnated vanadium on zeolite. Fig. 5 shows the energy per mol of *i*-Pam calculated from integration of DSC curve in the temperature range of the reaction as a function of vanadium content on the zeolite.

Maesen and Hertzenberg [17] also used TGA to measure Brønsted acid sites in Y-zeolite, our result for the zeolite without vanadium matches very well theirs for a zeolite with a similar unit cell size. From Fig. 4, it is deduced that the quantity of Brønsted acid sites – that correspond to the *i*-Pam moles broken down – decreases linearly as vanadium concentration on zeolite increases. This is a direct evidence of acid sites neutralization by vanadium species suggested for the first time by Torrealba et al. [10], and used as a key step to explain the action of vanadium on Y-zeolite by Trujillo et al. [7]. As vanadium was deposited on the external surface of the zeolite, from Fig. 4 one can also deduce that vanadium was able to move on the zeolite surface to reach acid sites, and that movement did not require the presence of steam. When organic matter is burned at 573 K vanadium remains in the external part of zeolite [7] and the sample is highly colored (red brick) but as temperature increases samples decolorize becoming white at 993 K. This change in color means a depolymerization reaction and metal migration on the surface, as most of the zeolite surface is internal surface, we deduce that vanadium migrates to the inner part of the structure.

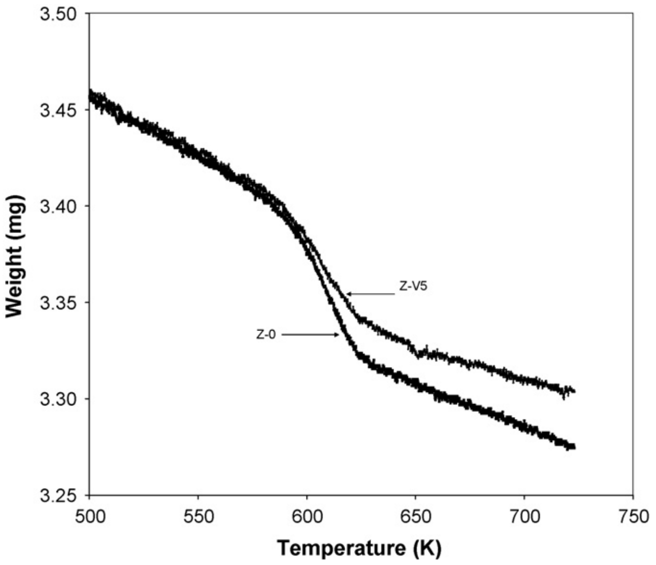

Fig. 3. TGA for the samples without vanadium (Z-0) and with vanadium (Z-V5).

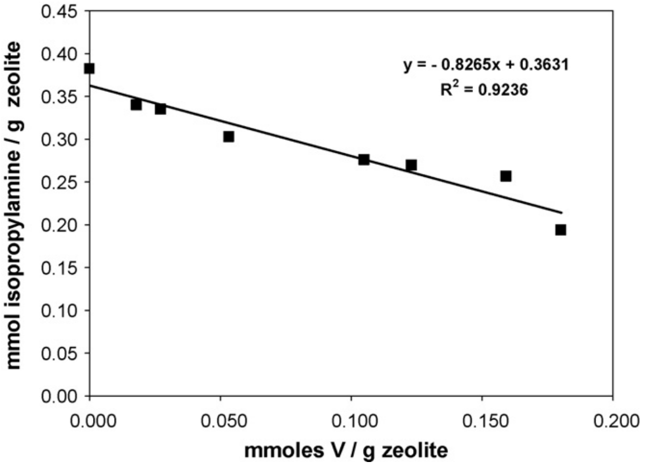

Fig. 4. Quantity of isopropylamine decomposed by a gram of zeolite as a function of vanadium loading.

The slope of the straight line obtained in Fig. 4 allows us to speculate about the size of vanadium species that neutralize acid sites on Y-zeolite. If vanadium neutralizing species contain one single vanadium atom the slope would be −1.0, if they contain two vanadium atoms the slope would be −0.5. The value −0.82 is near −1 but leaves open both possibilities, however, *i*-Pam cannot reach all acid sites in Y-zeolite, the amine only enters

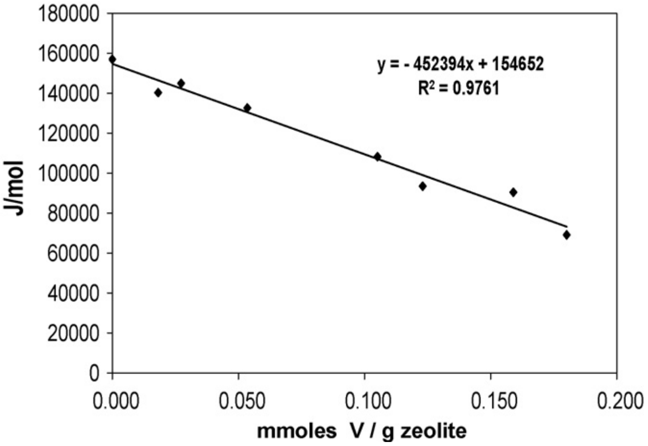

Fig. 5. Reaction heat plus desorption heat of the products for each mol of isopropylamine as a function of the quantity of vanadium on a gram of zeolite.

zeolite's supercages [17]. If monoatomic vanadium species were able to neutralize acid sites in hexagonal rings or in sodalite cages, those atoms would not be counted by the isopropylamine test and our test would give a less negative slope. This analysis leads us to propose that the neutralizing specie contains only one vanadium atom, probably VO_2^+ as was proposed by Trujillo et al. [7].

Fig. 5 shows DSC peak integration as a function of the vanadium concentration in zeolite. The reaction is endothermic and it is observed that the energy absorbed by each mol of *i*-Pam decreases linearly as vanadium concentration on zeolite increases. To understand the meaning of the graph we should be aware that the peak represents the energy absorbed in the amine decomposition reaction and the energy required to desorb reaction products from the surface of the catalyst. Reaction enthalpy is a state function and therefore independent of whether the reaction is carried out in presence or absence of a catalyst; consequently if it is observed that the energy detected by the DSC decreases as a function of vanadium concentration, it is necessary to conclude that as the amount of vanadium increases less energy is required to desorb reaction products from the surface.

The catalyzed reaction involves minimum three steps: amine adsorption, reaction and products desorption. Amine adsorption will always be exothermic as well as reaction products desorption will always be endothermic. The peak that appears between 589 and 635 K represents the last two steps of the process: reaction and desorption, in this case both are endothermic. The analysis of the energy diagram versus reaction coordinate for the catalyzed way allows concluding that when vanadium concentration in zeolite increases, products desorption progressively requires a smaller amount of energy. If desorption requires less energy it is because less energy is released in the exothermic step of the amine adsorption. In other words, Fig. 5 tells us that when vanadium concentration on zeolite increases less energy is released when *i*-Pam adsorbs on zeolite's acid sites.

It is recognized in the literature that zeolites have acid sites of different strength and a way to differentiate their strength is from the energy release when these sites are neutralized by bases such as ammonia or pyridine. Fig. 5 shows us that the energy released in *i*-Pam adsorption on Y-zeolite decreases as vanadium concentration increases, a possible explanation would be that vanadium selectively neutralizes the sites where more energy is released by the reaction with *i*-Pam; that means that vanadium neutralizes preferentially the strongest acid sites in the catalyst. Vanadium (V) is amphoterous but as the metal is in its highest oxidation state its behavior is more acid than basic, so in the reaction with zeolite only the strongest acid sites have the potential to make vanadium(V) behave as a base. Selective neutralization of the strongest acid sites in the catalyst is a fundamental hypothesis of the mechanism proposal for the destruction of zeolite by vanadium outlined without experimental confirmation, by Trujillo et al. [7].

4. Conclusions

The reaction of isopropylamine decomposition can be quantitatively followed by a simultaneous DSC–TGA analyzer. When this reaction was used to characterize vanadium contaminated Y-zeolite samples results show that vanadium is able to reach and neutralize acid sites. Vanadium neutralizing species probably contain only one vanadium atom. Results also show that vanadium has a preference for those sites where more energy is released when isopropylamine chemisorbs on the zeolite surface probably the strongest acid sites of the catalysts.

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