

DIFFERENTIAL SCANNING CALORIMETRY PROBES ACIDITY STRENGTH DISTRIBUTION IN CATALYTIC MATERIALS

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ABSTRACT

Differential scanning calorimetry (DSC) effects obtained with some catalytic solids such as amorphous silica-alumina and γ -alumina appear as an endothermic peak in the lower temperature region in a DSC thermogram, while desorption of presorbed triethylamine (TEA) from the acid sites of these solids appears as exothermic peaks in a higher temperature region. Other materials such as zeolites show a number of endothermic water-desorption peaks or a broad band covering a wide temperature range that crucially interfere with TEA-desorption peaks, and a precise evaluation of the acidity distribution in these materials is impossible. In the present work, an easy solution to this problem is found by nullifying the DSC effects caused by water desorption from the catalytic solid itself and only TEA-desorption peaks appear in the thermogram. The advantages of this DSC method over others are mentioned.

INTRODUCTION

The acidity distribution in catalytic materials is measured by several methods. The most common comprises titrations with n-butylamine in the presence of coloured indicators covering a whole range of pK_a [1]. However, this method gives results that depend on the amount of indicators, particle size of catalyst, concentration of titrant and the time allowed for n-butylamine equilibration [2,3]. An alternative method [3] chemisorbs bases having different pK_a values. These titrations cannot be used for dark catalysts.

IR spectra of presorbed pyridine have been measured to differentiate between Brönsted acid sites which form pyridinium ions (1540 cm^{-1}) and Lewis sites (1455 and 1459 cm^{-1}) on a catalyst surface [4–6]. Also pyridine-presorbing catalysts have been evaluated at successively increasing temperatures and followed by the measurement of their IR spectra [7,8]. Similarly, temperature programmed desorption (TPD) of pyridine previously adsorbed on a catalyst depends on the fact that the strongest acid sites are those which desorb pyridine at the highest temperature, and thus a rough quantitative evaluation of the distribution of the acid sites can be obtained [8,9].

However, this method uses a mass spectrometer as the ideal detector, measuring the composition of the effluent stream. Also, catharometric detection can be used but the high carrier flow rate required for desorption was found to be proportional to the rate of desorption [10].

The method suggested in this work simply uses a DSC thermal analyser whereby differentiation between physically and chemically adsorbed phases of a presorbed base is clearly accomplished. This method uses our previous idea of applying differential thermal analysis [11] as an acid strength probe for zeolite (mordenite) catalysts.

EXPERIMENTAL

The catalytic materials under study are γ -alumina (BDH), amorphous silica-alumina (Ketjen), silica gel (Davison) and three natural zeolites (Norton) named by their producer as zeolons. Table 1 gives some characteristics of these zeolons.

Preparations

TEA-presorbing solids. The catalytic materials were powdered in an agate mortar, heated at 500°C for 2 h and left to cool in the furnace down to 80°C, then thoroughly mixed while hot with excess TEA and left to soak overnight. The sample was filtered and dried at 60°C for 1 h before taking DSC measurements.

TEA-free solids. The catalytic materials were powdered, heated at 500°C for 2 h then left to cool in a desiccator.

DSC measurements

Conventional procedure. The sample cell (an aluminium crucible) contained an accurately weighed quantity of a TEA-presorbing solid (around 10 mg). The reference cell was an empty aluminium crucible.

TABLE 1

Characteristics of natural zeolons

Name	Mineralogy	No. of rings	Crystalline void volume (cc/cc)	Dominant cations
Zeolon 400	Clinoptilolite	10	0.34	K, Na
Zeolon 500	Chabazite/ erionite	8	0.47	Ca, Na
Zeolon 700	Ferrierite	10	0.28	K, Mg, Na

Modified nullifying procedure.

As above, the sample cell contained around 10 mg of a TEA-presorbing solid. The reference cell contained an equal weight of the same solid material (TEA-free). It has been found that the best results are obtained when the sample cell contains 10.2 mg and the reference cell contains 10.0 mg of TEA-presorbing and TEA-free materials respectively. Differences in weight up to 0.3 mg are tolerable.

All DSC measurements were carried out at atmospheric pressure and no purge gas was used. A Mettler DSC-30 thermal analyser (system TA 3000) was used under the following conditions: initial temperature, 50 °C; rate, 20 K min⁻¹; final temperature, 600 °C; plot, 10 cm; full-scale range, 25 mW; mass, 10.2 mg.

RESULTS AND DISCUSSION

The presorption of TEA on the catalytic materials was carried out as mentioned in the experimental section. This process was then followed by the gradual thermal desorption of TEA in the DSC cell instead of using a special reactor system as in the TPD method [8,9]. The DSC thermogram obtained records thermal effects partly due to water-desorption from the catalytic material itself as well as effects due to the desorption of TEA. The thermal effects appear in the thermogram as peaks, whose magnitude is proportional to the ΔH of desorption that can be determined via any of the available programs using the DSC unit. The ΔH determined for a given peak in the thermogram can thus be used to correlate the quantity of TEA (or any other base) that desorbs from a given group of acid sites having a definite acid strength. Hence, the acid strength distribution of solid catalytic materials can be evaluated. (Quantitative evaluations are being investigated and will be published later.) However, the peak temperature in the thermogram will be indicative of the strength of the group of acid sites responsible for this peak. The application of a kinetic program supplies values for the activation energy of desorption that assists in correlating the strength distribution of acid sites, since stronger adsorption (and desorption) requires larger activation energies.

For certain catalytic materials, e.g. γ -alumina and amorphous silica-alumina, whose water-desorption is accomplished in a temperature range outside the range characteristic of the presorbed amine, the conventional technique employed for any DSC measurement can be safely applied and a reasonable amount of information on the acidity distribution may be obtained. Figure 1 depicts such non-interfering DSC effects. An endothermic water-desorption peak appears between 60 and 200 °C with a maximum at 120 °C which is completely separated from the TEA-desorption peaks appearing between 200 and 400 °C with a maximum at 270 °C and between

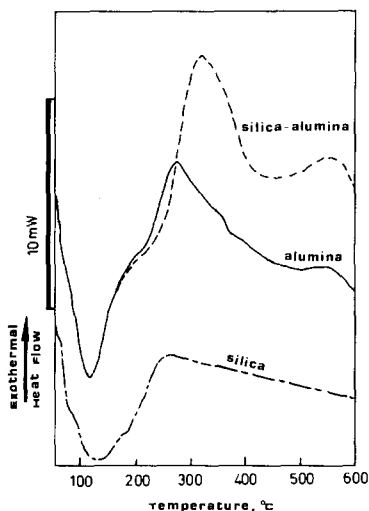


Fig. 1. DSC-thermograms for TEA-desorption from silica, alumina and silica–alumina using the conventional procedure.

480 and 600 °C with a maximum at 560 ° in the case of γ -alumina. Also, in the case of amorphous silica–alumina, the water-desorption peak is exactly similar to that in the case of alumina, whereas the TEA desorption peaks occur between 230 and 600 °C with two maxima, one at 320 °C and the other at 560 °C. It is evident that the number of acid sites in silica–alumina is greater than in alumina, the stronger sites appearing at 560 °C. Moreover, the exothermic peak due to the less strongly adsorbed TEA indicates stronger acid sites in silica–alumina (320 °C) than in alumina (270 °C). The TEA desorption peaks present in the DSC thermograms in the exothermic direction should indicate chemical adsorption on acid sites. Nevertheless, although silica gel does not contain any surface acidity, its DSC thermogram is given in Fig. 1 for comparison since silica is an important catalytic material. The TEA-desorption peak is endothermic and overlaps the water-desorption peak indicating the presence of only physical adsorption of TEA on silica.

However, catalytic solids such as zeolites whose water-desorption effects are found to cover a relatively wide temperature range (Fig. 2), cannot be investigated using the DSC conventional technique of measurement since the intrinsic effects of the zeolites will interfere with TEA-desorption effects. From Fig. 2 it may be concluded that the water capacity of the natural zeolites under investigation (Table 1) can be arranged in the order: Zeolon-500 > Zeolon-400 > Zeolon-700. For such zeolites, the modified nullifying procedure (see experimental section) is adopted to nullify the water-desorption effects (and any other effect) due to the zeolite itself such that the effects due to TEA-desorption only will appear in the thermogram.

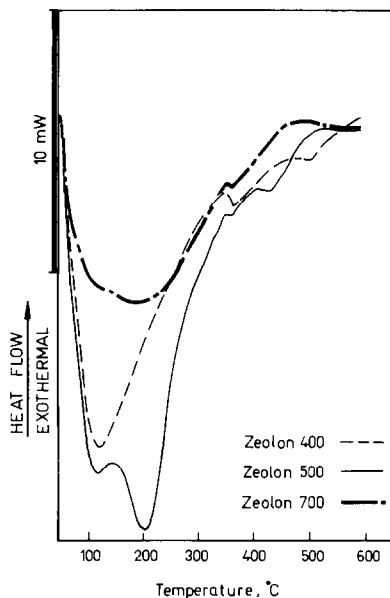


Fig. 2. DSC thermograms for natural zeolites (TEA-free).

Figure 3 shows the DSC thermograms obtained for a blank experiment in which both reference and sample cells are empty aluminium crucibles and for another experiment in which both reference and sample cells contain Zeolon-400 (10.0 mg). The two thermograms are found to be very similar and devoid of any peaks. This compensating procedure has also been examined for all the catalytic materials under investigation and in each case a thermogram similar to those shown in Fig. 3 was obtained. This finding proves that the DSC thermogram obtained using the modified nullifying procedure will only include peaks attributed to TEA-desorption from the

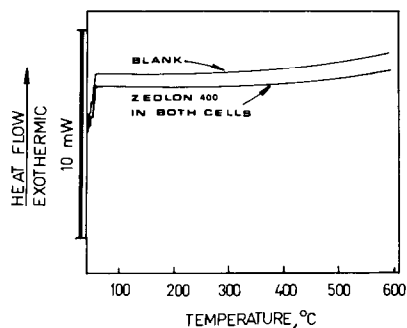


Fig. 3. DSC thermograms for blank experiment and for Zeolon-400 using the nullifying procedure.

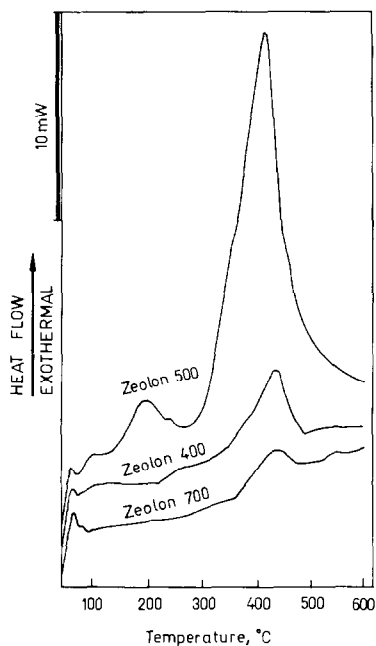


Fig. 4. DSC thermograms for TEA-desorption from the natural zeolites using the nullifying procedure.

solid catalytic surface and a clear idea about the acid strength distribution in these catalytic materials can be obtained.

Figure 4 shows the DSC thermograms obtained for TEA-desorption from the three zeolites under study using the modified nullifying procedure. The thermograms indicate that the acid strength distribution in the three zeolites may be generally similar but the numbers of the acid sites are widely different. Two types of acid sites appear to be present in the three zeolites; a small number represented by a peak with a maximum at around 200 °C whereas the majority of the acid sites is represented by a peak with a maximum at about 420 °C. The total ΔH values obtained for TEA-desorption from all acid sites in Zeolon-400, Zeolon-500 and Zeolon-700 are respectively 66, 596 and 28 J g⁻¹. For Zeolon-500, ΔH is 37.4 J g⁻¹ for the 200 °C peak and 558.4 J g⁻¹ for the 420 °C peak. This may indicate that the relative amounts of acid sites in Zeolon-400, Zeolon-500 and Zeolon-700 are 2.36, 21.25 and 1.0 respectively. A comparison of Figs. 2 and 4 may indicate that the natural zeolites possessing a larger water-adsorption capacity also possess a larger number of acid sites.

Figure 5 again shows the DSC thermograms of TEA-desorption from silica gel, γ -alumina and amorphous silica-alumina after nullifying the effects produced by each of these catalytic solids using the modified technique mentioned above. It is evident that silica can physically adsorb TEA

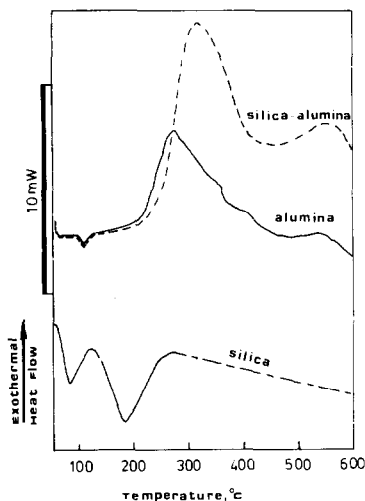


Fig. 5. DSC thermograms for TEA-desorption from silica, alumina and silica–alumina using the nullifying procedure.

into two modes since two peaks with maxima at 70 and 185 °C appear in the thermogram. The first peak may be attributed to desorption of TEA from the external surfaces of silica particles, whereas the second peak may be attributed to desorption of a larger quantity of TEA from the internal surface of the pores of silica. Figure 5 also shows that small quantities of TEA remain physically adsorbed by the silica–alumina and alumina; their peaks overlap the water desorption peaks of the solid materials appearing at 120 °C in the thermograms of Fig. 1. A comparison of Figs. 1 and 5 now shows that the large shouldered peak of Fig. 1 (silica) consists of three overlapping peaks; one with a maximum at 120 °C, is due to water desorption and the other two peaks with maxima at 70 and 185 °C, are due to physically adsorbed TEA, as mentioned above.

It may be of interest to note (Fig. 6) that $\log \Delta H$ for the desorption of chemically adsorbed TEA in the zeolons studied gives a linear relationship with the sum of the alkali metal oxide contents ($\text{Na}_2\text{O} + \text{K}_2\text{O}$) as well as with the crystalline void volume in the zeolites. It may be presumed that the total acidity of these zeolites increases logarithmically with decreasing alkali metal oxide content and with increasing crystalline void volume.

The DSC method under investigation, though possessing the general characteristic of the TPD method, i.e. the desorption of a base from stronger acid sites taking place at higher temperatures than that from weaker acid sites, appears to have two main advantages: (a) the DSC method completely excludes the effects produced by the solid adsorbent, whereby the effects produced by the base desorption only appear in the thermogram obtained; (b) the DSC method differentiates between the physical and chemical

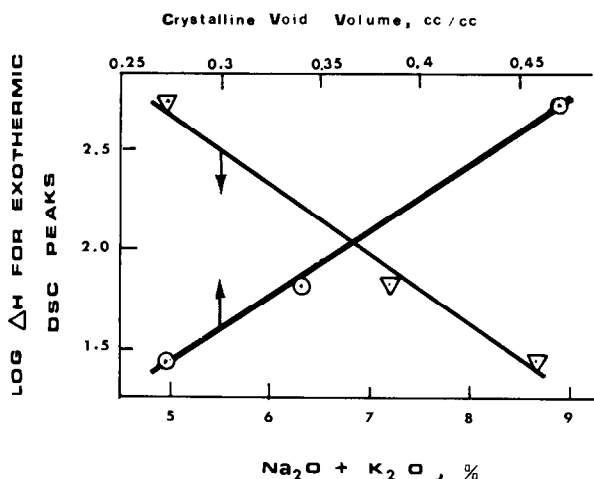


Fig. 6. Plots for the crystalline void volume and $\text{Na}_2\text{O} + \text{K}_2\text{O}$ content of natural zeolites vs. ΔH for the exothermic TEA-desorption peaks in thermograms using the nullifying procedure.

adsorption of the base which appear as endothermal and exothermal peaks respectively.

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