Thermochimica Acta, 129 (1988) 301–307
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

A STUDY OF HEAT-TREATED AMMONIUM-ION-EXCHANGED ZEOLITES BY DIFFERENTIAL SCANNING CALORIMETRY

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(Received 29 September 1987)

ABSTRACT

Ammonium-ion-exchanged forms of some zeolites were prepared from their cationic forms via exchange with NH_4NO_3. The resulting forms were dried, then heated in air for 1/2 h at 350, 400, 450, 500 or 550 °C, before analysis using differential scanning calorimetry (DSC) throughout a range of 50–600 °C without using any purge gas. The DSC thermograms obtained revealed the presence of several modes of binding forces between NH_4^+ and the zeolites. These forces differ from one zeolite to another in strength and quantity. Strongly bound NH_4^+ ions thermally decompose to NH_3 then to water, whereas weakly bound NH_4^+ ions decompose only to NH_3.

INTRODUCTION

Recently, many zeolites in their hydrogen forms have been used as highly active industrial acidic solid catalysts, particularly, in the processes of oil-dewaxing. The British Petroleum (BP) Co. and Mobil Oil Co. are employing catalysts containing hydrogen-mordenite [1] and hydrogen-ZSM-5 [2] in their catalytic dewaxing processes. The H-forms of zeolites can be prepared from their cationic forms by exchanging with hydrochloric acid [3] or with ammonium chloride [4,5] or ammonium nitrate solutions [6] followed by deammoniation at approx. 550 °C. Nevertheless, the modes of different binding forces between NH_4^+ and zeolites have not been investigated. The present work includes a study of the stepwise deammoniation of some NH_4-zeolites to compare their NH_4^+ bondings using DSC.

EXPERIMENTAL

Zeolites. Four zeolite types of the Zeolon series, Norton, Ohio, designated as zeolons 400, 500, 700 and 900, in their cation-forms, have been exchanged

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0040-6031/88/$03.50

with NH_4NO_3 solution as in ref. 6. Zeolons 400, 500 and 700 are natural zeolites, whereas zeolon 900 is synthetic. *Heat-treatment of zeolites*. Each NH_4-exchanged-zeolon was dried overnight at 120 °C then divided into five portions which were heated for 1/2 h in a muffle furnace at 350, 400, 450, 500 or 550 °C. The samples were directly analysed by DSC. *DSC measurements*. A Mettler DSC-30 unit (TA-3000) was used without purging gas (in air atmosphere). The sample cell of the DSC system contained a heat-treated NH_4-zeolon, whereas the reference cell contained corresponding cationated forms. DSC runs were at 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 mg. The nullifying technique adopted recently by the author [7,8] for DSC analysis of zeolites was used in measurements. The sample and reference cells contained equal weights.

RESULTS AND DISCUSSION

The modified nullifying technique adopted by the author and coworkers for DSC measurements of the acidity distribution of zeolites [7] and high

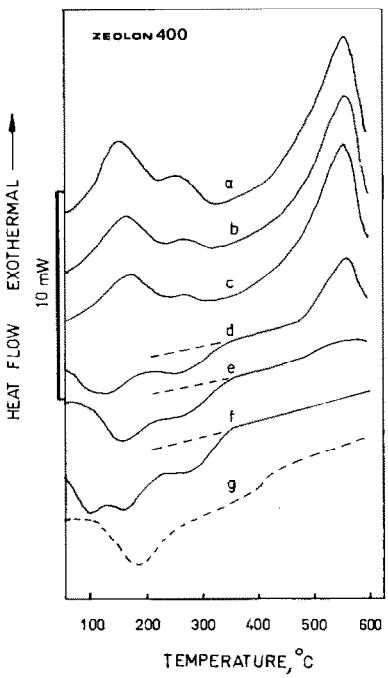


Fig. 1. DSC Thermograms of Heat-Treated NH_4-Zeolon 400. (a) Dried at 120 °C overnight, (b) heated at 350 °C for 1/2 h, (c) heated at 400 °C for 1/2 h, (d) heated at 450 °C for 1/2 h, (e) heated at 500 °C for 1/2 h, (f) heated at 550 °C for 1/2 h, (g) heated at 550 °C for 4 h.

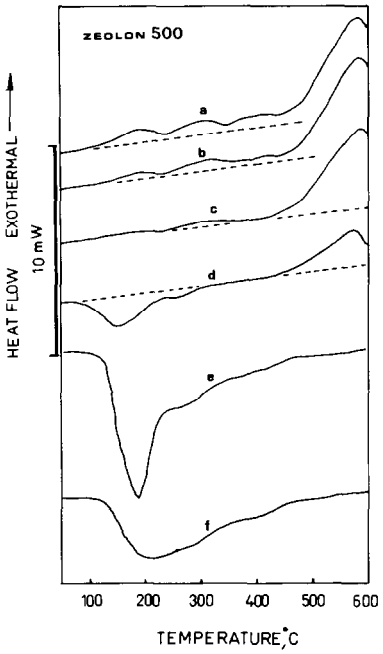


Fig. 2. DSC Thermograms of heat-treated NH_4-zeolon 500.

precision water determination of zeolites [8] is used to exclude any DSC effects caused by zeolitic water and constitutional changes. Using this technique in the present study reveals the dissociation of NH_4^+ from the zeolites under study as exothermal peaks, and the dehydroxylation of the hydrogen form subsequently produced as endothermal water peaks in the DSC thermograms obtained. If the conventional DSC technique is used (reference cells always empty), the DSC effects due to the zeolite itself overlaps the NH_3 and H_2O effects obtained through the thermo-decomposition of the ammonium-exchanged zeolons. However, the conventional DSC procedure has been successfully used for measuring acidity distribution in alumina and silica–alumina [9].

Close similarities are seen when comparing the DSC thermograms obtained for the four heat-treated ammonium-exchanged zeolons under study (Figs. 1–4). The thermograms obtained for one zeolite (NH_4-zeolon 400) are considered to reveal the general response of ammonium-exchanged zeolons towards short-period (1/2 h) heat-treatment in the range 350–550 °C, before the DSC measurements (Fig. 1).

Thermogram (a) in Fig. 1 was obtained for zeolon 400 in its NH_4-form after being dried overnight at 120 °C; three exothermic peaks with maxima at 150, 225 and 560 °C appear, which indicates that NH_4^+ ions are bound to the zeolitic structure of zeolon 400 in three different modes of varying strengths. Evidently, the 150 °C-maximum peak represents the weakest

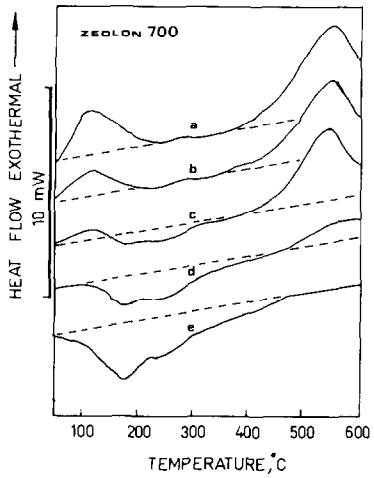


Fig. 3. DSC Thermograms of heat-treated NH_4-zeolon 700.

NH_4^+ binding forces, whereas the 560 °C-maximum peak represents the strongest NH_4^+ bonding. Thermograms (b) and (c) in Fig. 1 show the DSC effects obtained for NH_4-zeolon 400 after drying overnight at 120 °C followed by heating in a muffle-furnace in air atmosphere for 1/2 h at 350 and 400 °C, respectively. The two first peaks decrease in magnitude and

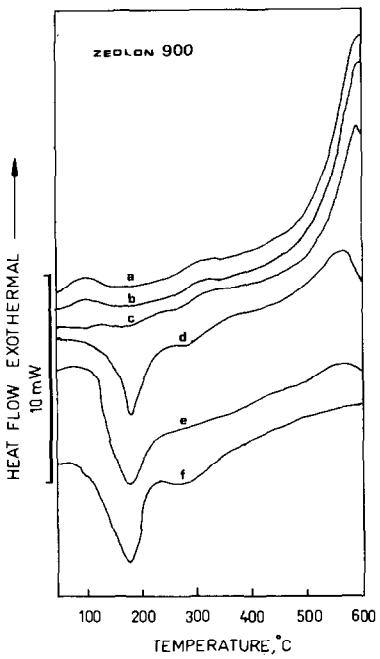


Fig. 4. DSC Thermograms of heat-treated NH_4-zeolon 900.

suffer a slight shift of their maxima to higher temperatures as a function of increasing the muffle heat-treating temperature. This may be attributed to dissociation of some less-strongly bound ammonium ions of the modes represented by these two peaks. Nevertheless, the 560 °C-maximum peak does not suffer any change either in magnitude or in its temperature position in the thermogram. This indicates that the NH_4^+ ions represented by the 560 °C-maximum peak in NH_4-zeolon 400 are completely stable toward heating up to 400 °C.

Thermogram (d) in Fig. 1, obtained for the heat-treated NH_4-zeolon 400 at 450 °C for 1/2 h, shows complete disappearance of the two low-temperature exothermal peaks and partial decrease in the area of the 560 °C-maximum peak representing strongly bound NH_4^+. Moreover, two endothermal water-desorption peaks with maxima at around 130 and 250 °C appear in thermogram (d).

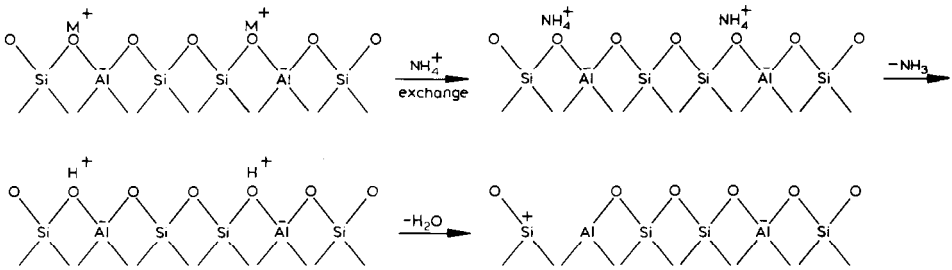
Thermograms (e) and (f) in Fig. 1 show that only a small amount of strongly-bound NH_4^+ remains in NH_4-zeolon 400 after heating at 500 °C for 1/2 h, while the water-desorption peaks increase in area and shift to higher temperatures. Heating this ammonium-zeolon at 550 °C for 1/2 h results in the complete disappearance of the 560 °C-maximum NH_3-desorption peak and the appearance of three endothermic water-desorption peaks with larger areas.

Thermogram (g) was obtained for NH_4-zeolon 400 after heating at 550 °C for 4 h. A large peak with a maximum at around 200 °C and a shoulder ending by 400 °C appeared as endothermal water-desorption DSC effects at higher temperatures than in thermograms (d), (e) and (f).

The above study on NH_4-zeolon 400 indicates the presence of weakly- and strongly-bound NH_4^+. The DSC peaks due to weakly-bound NH_4^+ decrease in area without the appearance of any water peaks, whereas the DSC peak due to strongly-bound NH_4^+ (maximum at 560 °C) decreases in area on heating from 400 to 450 °C, this decrease being associated with the appearance of some DSC water effects. This may indicate that weakly-bound NH_4^+ ions are not attached to framework oxygen in the zeolon structure (no water effects appear), whereas strongly-bound NH_4^+ are attached to framework oxygen (water effects appear). Since zeolites may contain a larger number of metal cations than that calculated per unit cell [10], some of these cations will not be involved in cation–oxygen bonds; on ammonium exchange for these cations the ammonium ions by turn will not be involved in NH_4^+–oxygen bonds; and on deammoniation no hydroxyl groups are produced and no water is formed by heating. On the other hand, cation–oxygen bonds produce on ammonium exchange NH_4^+–oxygen bonds which dissociate on heating to give NH_3 and surface hydroxyl groups which dehydroxylate to give H_2O on further heating as shown below.

Also, it has been found that in complex or isolated group structures of zeolites, shared oxygen atoms do not lie near metal cations [11,12], which

may be indicative of the absence of water formation after deammoniation.



Although the general behaviour of the four ammonium-zeolons under study is similar, there are some differences in the thermograms given in Figs. 1–4. Figures 1 and 3 indicate that NH_4-zeolons 400 and 700, respectively, possess an appreciable portion of their ammonium ions weakly bound to the zeolitic structure, whereas zeolons 500 and 900 (Figs. 2 and 4, respectively) exhibit much lower proportions of such weakly-bound NH_4^+. Moreover, zeolon 700 possesses one (weaker) type of weakly-bound NH_4^+, whereas zeolon 400 possesses two types. On the other hand, strongly-bound NH_4^+ in the four zeolons dominate and can be arranged according to their zeolons in a quantitative order: zeolon 900 > zeolon 400 > zeolon 500 $\geqslant$ zeolon 700. However, quantitative evaluation of ΔH which gives numerical values for the relative amounts of NH_4^+ in the four zeolons under study is impossible because the DSC effects for strongly-bound NH_4^+ require temperatures beyond 600 °C which are not available to the DSC-30 unit employed [7]. Comparing the strength for NH_4^+ linkage to the zeolons investigated, it was decided to take the peak-maximum temperature as the indicator [13]. On this basis, the order of NH_4^+ strength can be arranged according to the zeolons: zeolon 900 > zeolon 500 > zeolon 400 $\geqslant$ zeolon 700.

Deammoniation and dehydroxylation of NH_4-zeolon 700 look much easier than these reactions for any other zeolon investigated, since endothermic water desorption effects appear in thermogram (c) of Fig. 3 where the sample was only heated at 400 °C for 1/2 h before DSC measurement.

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