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APPLICATION OF THE THERMO-GAS-TITRIMETRIC TECHNIQUE FOR THE ESTIMATION OF AMMONIA CONTENT IN AMMONIUM EXCHANGED ZEOLITES *

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ABSTRACT

The application of the thermo-gas-titrimetric (TGT) technique for estimating the ammonia content in ammonium X-, Y- and L-type zeolites is described. The values of ammonia content in different zeolites determined by the TGT method are in good agreement with those obtained by other conventional methods. The use of the TGT method enables one to distinguish between the ammonium ions physically adsorbed and those exchanged by the zeolite. The details of this method and its specific advantage are described in detail.

INTRODUCTION

The thermochemical properties of ammonium-exchanged zeolites have been investigated due to their extensive use as catalysts [1—3]. Zeolites are generally exchanged with ammonium ions prior to their use in acid-catalyzed reactions. The decomposition of ammonia from ammonium zeolites will generate acidic sites in the zeolites [4,5]. Several workers [6—8] have shown a linear correlation between the degree of ammonium exchange, acidic and catalytic properties of the zeolites. To investigate such correlations and also to understand the catalytic properties of ammonium-exchanged zeolites, knowledge about the exact ammonia content in ammonium-exchanged zeolites is most essential. The percentage of ammonia content in ammonium zeolites is generally determined by estimating the amount of Na and K ions (equivalent to NH_4^+ ions) eluted during ion exchange by gravimetric or flame photometric analysis. In the present work, the application of combined derivatographic and thermo-gas-titrimetric (TGT) techniques developed by Paulik and Paulik [9] is reported for the estimation of ammonia content in ammonium-exchanged zeolites of X-, Y- and L-type. The advantage of this method is also outlined.

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EXPERIMENTAL

Materials

The starting zeolites, Linde SK-40 (NaY), 13X(NaX) and SK-45 (KL), were obtained from the Linde Division, Union Carbide Corporation. The unit-cell composition of the initial NaX, NaY and KL zeolites is $Na_{86}(AlO_2)_{86}$, $(SiO_2)_{106}$, $Na_{56}(AlO_2)_{56}$, $(SiO_2)_{136}$, and $K_9(AlO_2)_9(SiO_2)_{27}$, respectively. Ammonium forms of X-, Y- and L-zeolites were prepared by successive exchanges with 10% aqueous NH_4Cl at reflux temperature. The samples were then filtered, washed until no chloride ion was detected in the filtrate and finally dried at 110°C. Six samples with different contents of ammonia were prepared. The extent of ion exchange with NH_4^+ ions was determined by estimating the Na and K eluted during ion exchange by gravimetric and flame photometric analysis. The unit-cell composition of the six samples prepared and the percentage ammonia content in these samples represented as $(NH_4)_2O$ are given in Table 1.

Apparatus

The principle and the details of the combined derivatography were described in detail by Paulik et al. [10] in an earlier communication [10,11]. The combined derivatographic and thermo-gas-titrimetric device is an additional facility developed by Paulik et al. [10] to estimate the amount of acidic or basic decomposition products. In this technique, the evolving gaseous products during the thermal decomposition of the solid are quantitatively transported into an aqueous absorbing solution by means of an inert carrier gas stream over the sample. The pH of the aqueous absorbing solution changes, depending on the acidic or basic nature of the gaseous products. Since the pH changes, the potential difference between the glass and calomel electrodes dipping into the solution will alter. An amplifier is coupled to the electrodes and this in turn is connected to an automatic burette. When the

TABLE 1

Thermo-gas-titrimetric (TGT) results of ammonia determination in various ammonium zeolites

Unit cell composition of zeolites	$(NH_4)_2O$ Content (%)		
	Flame photometry	Gravimetry	TGT Technique
$(Na)_{43}(NH_4)_{43}(AlO_2)_{86}(SiO_2)_{106}$	0.289	0.297	0.283
$(Na)_{28}(NH_4)_{28}(AlO_2)_{56}(SiO_2)_{136}$	0.303	0.328	0.297
$(Na)_{19}(NH_4)_{37}(AlO_2)_{56}(SiO_2)_{136}$	0.305	0.310	0.300
$(K)_{7.2}(NH_4)_{1.8}(AlO_2)_9(SiO_2)_{27}$	1.815	—	2.100
$(K)_{6.7}(NH_4)_{2.3}(AlO_2)_9(SiO_2)_{27}$	1.822	—	1.730
$(K)_{5.8}(NH_4)_{3.2}(AlO_2)_9(SiO_2)_{27}$	1.834	—	1.778

potential difference between the glass and calomel electrodes changes, the amplifiers coupled to the electrodes automatically keep the burette in operation. The burette feeds the titrant to the absorbing solution until the original value of the potential difference between the electrodes is regained. The slide contact of a potentiometer moves along with the piston of the burette, and the galvanometer coupled to the potentiometer records the thermo-gas-titrimetric (TGT) curve. The total amount of the titrant consumed will be obtained from the TGT curve.

The thermal analysis apparatus used in this study was a combined derivatograph and thermo-gas-titrimetric (Paulik—Paulik—Erdey) instrument made by MOM, Budapest, Hungary, which is able to record TG, DTG, DTA, T, TG and DTGT curves. When TGT is in use, the instrument is adjusted to record TG, DTG or DTGT, TGT and T curves.

RESULTS AND DISCUSSION

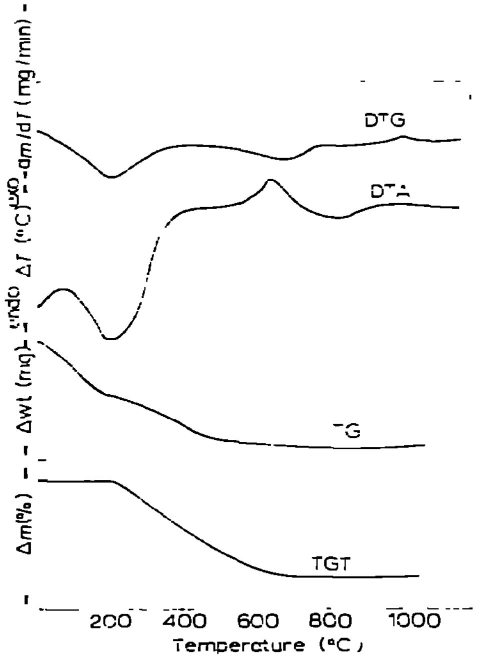
The thermal decomposition of ammonium zeolites in the presence of an inert gas may be represented by the following equation

$$NH_4Z(s) \rightarrow HZ(s) + NH_3(g)$$

where Z = X, Y or L type zeolite. Since the ammonia is liberated during the thermal decomposition of the zeolites in the above manner, it is considered worthwhile to apply the TGT technique to determine the ammonia content in ammonium-exchanged zeolites. Accordingly, the following procedure was standardized.

About 300 mg of the ammonium zeolite sample was placed in the platinum crucible (height, 16 mm; diameter, 14 mm) of the thermal analysis apparatus. The sample was heated up to 1000°C at a rate of 10°/min in the presence of N_2 as carrier gas with a flow rate of 20 l/hr. The ammonia gas liberated from the zeolite during the decomposition was absorbed into an absorbent consisting of 200 ml of distilled water with an ethanol content of 3%, and the absorbent was adjusted to pH 5 with 0.1 N HCl solution. The automatic burette of the TGT apparatus was filled with 0.1 N HCl test solution. Whenever the pH of the absorbent changed due to absorption of ammonia gas, the burette started to feed in the test solution (0.1 N HCl); from the total volume of the test solution consumed, the amount of ammonia decomposed from the zeolite was calculated using the factor that 1 ml of 0.1 N HCl solution will measure 1.073 mg of NH_3. From the amount of ammonia, the percentage of $(NH_4)_2O$ content in the zeolite was calculated. The same procedure was followed to determine the ammonia content for other samples of ammonium zeolites (X-, Y- and L-zeolites). The unit cell composition of the different zeolites and the values for the percentage of $(NH_4)_2O$ content obtained by this method are summerized in Table 1. The values of $(NH_4)_2O$ content obtained by other conventional techniques, such as flame photometry and gravimetry, are also given in Table 1 for comparison of the accuracy of the TGT technique. The results in Table 1 clearly show that the values of $(NH_4)_2O$ content in different zeolites determined by the TGT method are in good agreement with the values obtained by flame photometric and gravimetric methods.

The TGT, TG, DTA and DTG thermograms obtained for one typical ammonium-exchanged zeolite (NH_4KL) are given in Fig. 1. The weight loss shown by the TG curve up to 200°C is due to loss of physically adsorbed water. The TGT curve shows that the consumption of the titrant starts around 200°C and continues up to 680°C. This indicates that the decomposition of ammonia (deammoniation) occurs continuously between 200 and 680°C. The weight loss by the TG curve between 200 and 680°C can be ascribed to the deammoniation reaction. In agreement with the TG curve, the DTG curve shows two distinct peaks at 200 and 680°C, which can be ascribed to the removal of physically adsorbed water (200°C) and the deammoniation reaction (680°C). The DTA curve shows an endotherm at 200°C due to water desorption and a sharp exotherm at 650°C due to exchanged ammonia. These observations regarding the nature of the decomposition of NH_4KL zeolites are in accordance with those reported by earlier workers [2] Similar thermograms were obtained for other NH_4KL zeolites (Table 1) of different ammonia content



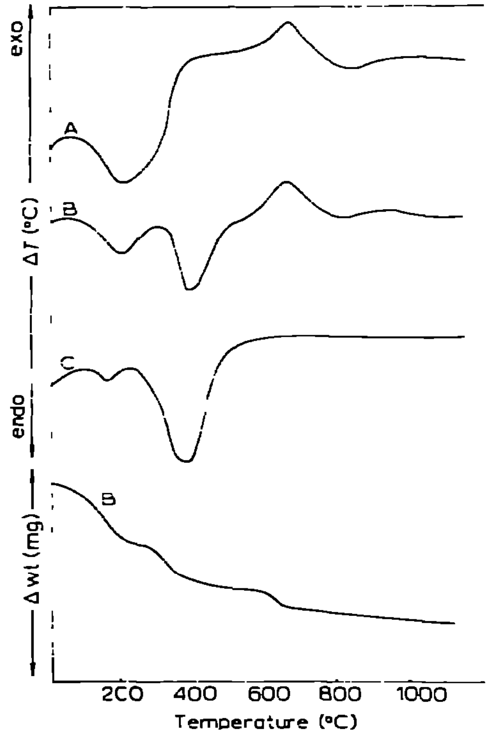


Fig 1 Thermograms of the combined derivatographic and thermo-gas-titrimetric (TGT) examination of NH_4KL

Fig 2 The DTA curves of NH_4KL Zeolite (Curve A), NH_4KL zeolite containing adsorbed NH_4Cl (Curve B), NH_4Cl (Curve C), and the TG curve of NH_4KL zeolite containing adsorbed NH_4Cl (Curve B').

Specific advantage of the TGT technique

The ammonia content in ammonium-exchanged zeolites is conventionally determined by estimating the amount of Na and K ions eluted during ion exchange by gravimetric or flame photometric analysis. Generally, aqueous NH_4Cl is used as a reagent to obtain ammonium-exchanged zeolites. During the exchange it is likely that a certain amount of NH_4Cl is absorbed on the zeolite or inside the cavities. Despite thorough washing of the zeolite, small amounts of the NH_4Cl may still be present on the zeolite. In the conventional methods adopted to determine the ammonia content in ammonium-exchanged zeolites it is not possible to verify whether any such adsorbed NH_4Cl is present on the zeolite. This is because the ammonia content is estimated by taking Na^+ or K^+ ions eluted during ion exchange into consideration, which accounts for the fact that ammonium ions exchanged though Na or K ions do not provide any information regarding NH_4Cl adsorbed on the zeolite However, by the application of TGT device it is possible to determine whether any such adsorbed NH_4Cl is present on the zeolite. To highlight this advantage, one sample of ammonium zeolite (NH_4KL) was prepared on which some amount of adsorbed NH_4Cl was present and the TG and DTA curves of this sample were recorded (Curve B, Fig. 2). In Fig. 2, the DTA curve (Curve A) of the same zeolite after thorough washing of the adsorbed NH_4Cl and also the DTA curve of the NH_4Cl (Curve C) are given to show the difference between the sample which contains adsorbed NH_4Cl and that which is free from adsorbed NH_4Cl. The DTA curve of the zeolite on which some adsorbed NH_4Cl is present (Fig. 2, Curve B) shows two endothermic peaks around 200 and 380°C and one exothermic peak at 650°C. The peak at 200°C may be ascribed to the loss of physically adsorbed water and the peak at 380°C is due to dissociation of NH_4Cl present in the zeolite in a physically adsorbed form. The peak at 650°C is due to oxidation of ammonia. The DTA curve of NH_4Cl (Fig. 2, Curve C) shows two endothermic peaks: one at 180°C and the other at 380°C. The peak at 180°C is due to transition from one crystalline form to another [12]. The peak at 380°C is due to dissociation of NH_4Cl. Since the DTA curve of NH_4Cl shows a peak at 380°C which is also present in the DTA curve of ammonium zeolite which contains physically adsorbed ammonium chloride, it can be inferred that this zeolite contains a proportion of adsorbed ammonium chloride. The peak at 180°C which is due to a crystalline phase transition would have also appeared in the DTA curve of ammonium zeolite containing adsorbed ammonium chloride, but this peak must have overlapped with the peak at 200°C which is ascribed to the loss of physically adsorbed H_2O on the zeolite. Interestingly, the peak at 380°C, which is due to dissociation of NH_4Cl, is absent in zeolite free from adsorbed NH_4Cl (Fig. 1, Curve A). The TGA curve of the ammonium zeolite which contains adsorbed NH_4Cl (Fig. 2, Curve B') also shows the weight loss in three steps. The first step up to 200°C is due physically adsorbed water, the second (200°—500°C) is due to dissociation of NH_4Cl along with decomposition of ammonia, and the third step (500—700°C) is due to complete decomposition of ammonia. The TG curve of the zeolite free from adsorbed NH_4Cl does not indicate three such distinct steps (Fig. 1). Thus TG and DTA curves clearly distinguish the difference between the ammonium zeolite sample which contains adsorbed NH_4Cl and which is free from adsorbed NH_4Cl. This is one specific advantage of using the TGT technique as a method for the estimation of ammonia content in ammonium exchanged zeolites.

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