JOURNAL OF CATALYSIS **43**, 346–352 (1976)

The Deammoniation Reaction of Ammonium Y Zeolite

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Received February 23, 1976

The deammoniation reaction of ammonium exchanged zeolite Y has been studied using differential thermal analysis. The results show deammoniation occurs in two endothermic steps: the first is dissociation of NH_3 from the small pore structure at 250°C, the second from large pore structure in the 300–400°C region. It implicates that the acid sites generated by this dissociation are weaker in the small pores than in the large pores. The results also demonstrate that a highly acidic solid such as Y zeolite need not give an exothermic peak upon removal of chemisorbed ammonia in oxygen-containing atmospheres if the ammonia is rapidly removed from the reaction zone.

INTRODUCTION

The deammoniation reaction of ammonium exchanged zeolite Y (NH_4Y) has been the subject of many differential thermal analysis (DTA) investigations (*1*–*4*). DTA used in conjunction with effluent gas analysis has been very useful to obtain not only information of physical and chemical changes but also the heat effects taking place in the deammoniation step. Such coupled and interlinked knowledge which can be used to elucidate the mechanism by which those changes generated, is of special interest in catalysis.

In the case of the deammoniation of NH_4Y, previous DTA results have unfortunately failed to demonstrate such capability. Due to the different gaseous atmospheres caused by inadequate equipment and improper operating conditions, the discrepancies among reported thermograms of NH_4Y have been widespread. Even general agreement as to whether such a reaction is endothermic or exothermic remains to be reached.

Earlier work by Venuto and co-workers (*1*) reported DTA profiles obtained in oxygen and nitrogen atmospheres for previously uncalcined NH_4Y. They associated the two intense exothermic peaks near 400 and 550°C recorded in oxygen with the loss of NH_3 in the zeolite. Similar exotherms, but of much weaker intensity were in the thermograms obtained in nitrogen atmosphere. Hopkins (*3*), however, found only one major exotherm in the 300–700°C region of the thermogram in both dry oxygen and dry nitrogen environment. Both authors gave no explanation of the nature of the exotherms in nitrogen. The exothermic peak in oxygen was attributed to intracrystalline oxidation of NH_3 (*1*). On the other hand, Ward (*2*) did not find any exothermic peak in his thermogram recorded in flowing helium. Recent work by Bolton and Lanewala (*4*) reported that their DTA thermogram in He consists of two endothermic peaks in the 100–400°C region and one exothermic peak at about 550°C for NH_4Y of SiO_2 to Al_2O_3 molar ratio of 5. They have attributed the second endothermic peak, starting at about 250°C, to the decomposition and evolution of NH_3. They proposed to assign the exothermic peak at 550°C to the formation of dehydroxylated species, because they realized that ". . . practically all of the ammonium cations have been decomposed and evolved by 400°C . . .".

We have carried out the DTA investigations of NH_4Y deammoniation in greater detail. In this paper, we present a self-consistent and what we believe to be the true thermogram of the deammoniation of NH_4Y under optimum conditions. The assignment of various endo- and exotherms to those corresponding reaction steps from which they are generated is proposed and examined. Discussion of reported discrepancies in the thermogram is also included.

EXPERIMENTAL METHODS

Apparatus and Procedure

An R. L. Stone differential thermal analyzer, Model DTA 202, was used with an SH-BE type sample holder. Platinel-II differential thermocouple was imbedded inside the reference substance and the sample cells to detect the temperature difference. A separate control thermocouple in the holder block was used to sense and program the temperature of the sample holder as a whole. Purge gases were directed from the bottom of the cells to flow through the sample and reference material at equal rate.

The operating conditions, unless otherwise specified, were as follows: A 10 mg sample was heated at a rate of 10°C/min, with purging gas N_2, O_2, or air flowing at the rate of 100 ml/min. The reference material was Vycor powder of 100–140 mesh size, being calcined at 1000°C for 0.5 hr.

Sample Preparation

The samples used in this study were prepared from pure synthetic Y type faujasite obtained from the Linde Division of Union Carbide. Four different cationic forms were prepared by ion exchange:

1. 96% exchanged NH_4Y: Synthetic NaY powder was exchanged repeatedly with 1 *N* NH_4Cl solution at 100°C. The final water-washed, chloride-free and oven-dried sample has the following unit cell composition;

$$(NH_4)_{52}Na_2Al_{54}Si_{138}O_{384}(H_2O)_x.$$

2. 65% exchanged NH_4Y: Synthetic NaY was exchanged with excess NH_4Cl solution at room temperature for 24 hr. The composition of the washed, dried sample is: $(NH_4)_{35}Na_{19}Al_{54}Si_{138}O_{384}(H_2O)_x$.

3. $CsNH_4Y$: A sample of 96% ammonium exchanged Y zeolite was exchanged with excess 0.1 *N* CsCl solution at room temperature. The water-washed, oven-dried product has a composition of:

$$Cs_{38}(NH_4)_{14}Na_2Al_{54}Si_{138}O_{384}(H_2O)_x.$$

4. $LaNH_4Y$: A sample of NaY was exchanged with excess 0.3 *N* $LaCl_3$ solution until about 70% of the Na in Y was replaced by La ions. The partially exchanged, water-washed and dried LaNaY was calcined in air at 550°C for 16 hr and then exchanged again with NH_4Cl solution. The final washed and dried product has a unit cell composition of:

$$La_8(NH_4)_{29}Na_1Al_{54}Si_{138}O_{384}(H_2O)_x.$$

RESULTS AND DISCUSSION

Thermogram in Inert Atmosphere

The thermogram of NH_4Y (96% exchanged) obtained in purified N_2 atmosphere is shown in Fig. 1. Up to 800°C there are only four endothermic peaks in the whole thermogram. The first endotherm reaches its maximum at about 150°C. The second one is much smaller than the first one and reaches its maximum at 250°C. The third endotherm is a diffuse one, ranging from 250 to 400°C, with a maximum probably at about 320°C. The last peak is at around 650°C. The small bump between 580–600°C is attributable to the reference material which is Vycor powder and should be ignored.

There are no signs of exothermic reactions. Based on effluent gas analysis, TGA

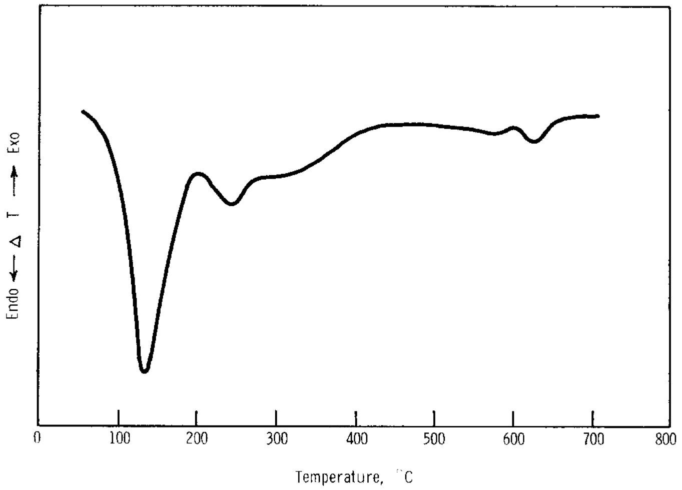

FIG. 1. DTA thermogram of NH_4Y (residual Na 0.2% wt).

and other experimental results to be mentioned later, we have assigned the endotherms to the following thermal reactions:

endo 1. At 150°C, desorption of physically adsorbed water from zeolite.
endo 2. At 250°C, dissociation of NH_3 from NH_4^+ in small pore system.
endo 3. Ranging from 250 to 400°C, dissociation of NH_3 from NH_4^+ in large pore system.
endo 4. At 650°C, dehydroxylation of HY.

The assignment of the first and fourth peaks agrees with most published data and we will not discuss these further. Excluding any complications, the decomposition of NH_4Y with inert gas purge may be represented by the following equation:

$$NH_4Y(s) \rightarrow HY(s) + NH_3(g)\uparrow.$$

The heat change should be endothermic on the basis of bond energy considerations. Our DTA thermogram with its endotherms confirms this point.

Crystallographically, there are two distinctively different cationic sites in Y zeolite according to Smith (*5*), namely, sites I and I′ in the small pore system and site II in the large pore system. It is not likely the dissociation of NH_3 from these different sites have the same energy change. We assign the second and third endotherms to reflect these changes.

It has been shown (*6*, *19*) that Cs ions are too large to enter the small pore system (sites I and I′) of Y through the 2.2 to 2.5 Å pore openings. Therefore, only NH_4^+ ions are located in the small pore of the $CsNH_4Y$ sample we prepared. The thermogram of this particular $CsNH_4Y$ sample is shown in Fig. 4. The absence of endo-3 demonstrates clearly that dissociation of NH_3 from the small pore sites is responsible for the endothermic reaction at 250°C. Applying a similar analysis, we have concluded that the third endotherm in the DTA thermogram of NH_4Y is associated with deammoniation in the large pore system. The location of NH_4^+ ions in the 65% exchanged NH_4Y and the $LaNH_4Y$ sample prepared in this study have been shown to be in the large pore system (*6*, *7*). DTA thermograms of both zeolite samples do not show distinctly the second endothermic peak (Figs. 2 and 3). There is no dehydroxylation peak in $LaNH_4Y$ but the exotherm for lattice collapse (1050°C) remains. These results demonstrate rather well the association of

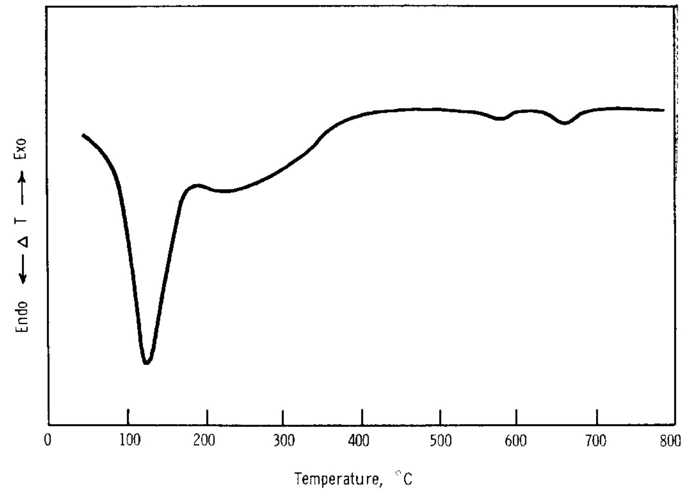

FIG. 2. DTA thermogram of partially exchanged NH_4Y (residual Na 3.2% wt).

the third endotherm with the deammoniation of NH_4^+ ions in the large pore structure (site II).

A DTA study deals with only very small samples, usually in the milligram range, therefore, it is advisable for us to verify this result on a macro scale. We have isothermally calcined 10 g of the 96% exchanged NH_4Y sample at 250°C for 4 hr in a constant N_2 flow. From the titration of NH_3 in the effluent gas and the analysis of the calcined solid, we found that only about 38% of the ammonium sites in the NH_4Y were decomposed after 4 hr. Furthermore, the remaining ammonium in the calcined sample can be easily replaced by Cs ion exchange, revealing the location of these ammonium ions to be in the large pores. The results are summarized in Table 1 and Fig. 5. The fact that ammonium in the large pores remains essentially localized at 250°C gives good support to our endotherm assignments. The approximate 40/60 ratio of small vs large pore

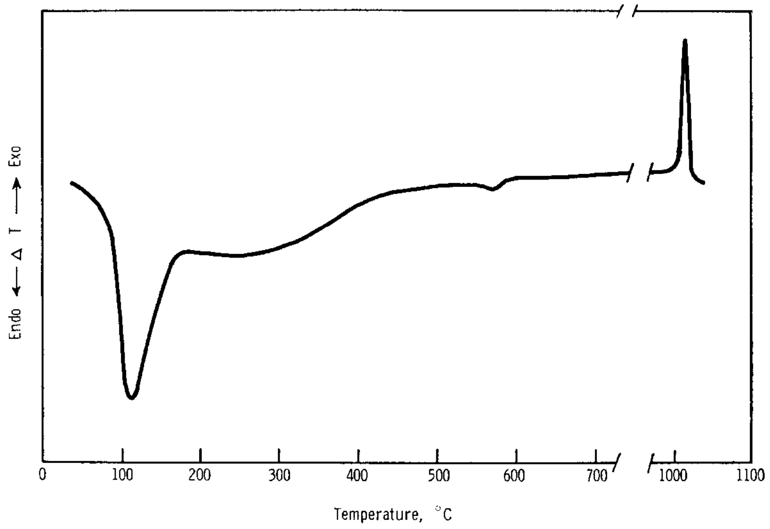

FIG. 3. DTA thermogram of $LaNH_4Y$.

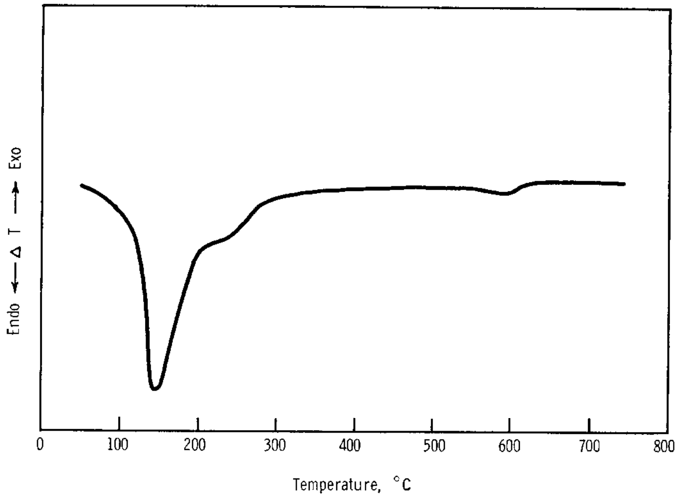

FIG. 4. DTA thermogram of $CsNH_4Y$.

sites is also in excellent agreement with the reported cation locations of dehydrated Y zeolite (*8*).

Origin of Exotherms

Various exothermic peaks beyond 400°C obtained in N_2 and He have been reported by many investigators (*1, 3, 4*). We attribute them to secondary reactions of decomposition products through improper operating condition; namely insufficient purge gas flow, too large sample sizes and others. Much DTA equipment does not have a dynamic purge gas system. Some equipment has purge gas which flows over the sample instead of through it. It has been shown that purge gas that flows over the sample holder cannot remove the evolved NH_3 and other decomposition products effectively (*4*). We have observed that insufficient gas flow may give similar unsatisfactory results. It removes effluent gas slowly and imcompletely and allows the back diffusion and mixing of room air into the sample site. Subsequent oxidation of ammonia gives rise of the exotherms. Low temperature catalytic oxidation of ammonia has been observed and reported (*9*). We have reproduced and then gradually reduced and eliminated the reported NH_4Y exotherms by increasing the flow of the purge gas and reducing sample size. On our equipment 10 mg and 100 ml/min appear to be the maximum sample weight

TABLE 1

The Composition of NH_4Y Samples

Description of sample	Atom ratio				SiO_2/Al_2O_3	Crystallinity[b]
	N/Al	H/Al[a]	Na/Al	Cs/Al		
NH_4Y (96% exchanged)	0.96	–	0.04	—	5.1	95
Above sample, after calcined at 250°C in N_2 for 4 hr	0.58	0.38	0.04	—	5.1	75
Above sample, after exchanged with 0.1 *N* CsCl	0.04	0.30	0.02	0.64	5.1	95

[a] Calculated by difference, assuming M/Al = 1.

[b] Based on initial crystallinity of NaY Sample.

and minimum gas rate to prevent the occurrence of exothermic peaks. The reported exotherms can also be eliminated, even under inadequate operating conditions, by providing an inert atmosphere shield, in addition to the purge gas over the sample holder, to protect against back diffusion of room air. We used a pressure dome which was supplied as accessories of R. L. Stone DTA-202 unit to cover the entire sample holder with a blanket of inert atmosphere.

As expected, other ammonium exchanged zeolites, such as mordenite (*10*), zeolite L (*11*) and erionite (*12*) also show only endotherms in their DTA thermograms in inert atmosphere.

Thermogram in Oxidizing Atmosphere

The DTA thermograms of NH_4Y obtained in air or oxygen by us appear not significantly different from those obtained in inert atmosphere. The fact that the thermogram stays unchanged despite the nature of the purge gas, inert or oxidizing, is not hard to comprehend. Although, several workers reported exotherms in air or oxygen beyond 400°C (*1, 3*). But it is a general established fact that deammoniation of NH_4Y is practically completed before 400°C (*2, 4*). Under our operating condition (high purge gas rate), decomposition of NH_4Y has been completed and evolving NH_3 gas has been purged out before the temperature becomes high enough to initiate the intracrystalline oxidation of ammonium cations as suggested by Barrer (*13*). Therefore, we believe that deammoniation of NH_4Y in oxidizing atmosphere may yield two distinctively different types of thermogram depending on the rate of purge gas flow. At high rate of purge, the thermogram will be similar to those obtained in an inert atmosphere, with endotherms only. At low purge gas rate, however, thermograms with exotherms will be obtained instead due to both intracrystalline and intercrystalline oxidation of ammonium groups left behind by insufficient purge. The latter case is the observation of Venuto *et al.* (*1*) and Hopkins (*3*).

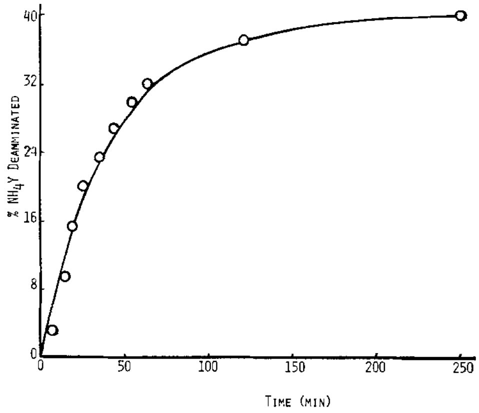

Fig. 5. Isothermal deammoniation of NH_4Y at 250°C.

Acidity of Sites

The dissociation of NH_3 from NH_4Y has been well established to be the mechanism to generate acid sites. Acidity of the sites generated and dissociation temperature of NH_3 are reflections of the bond energy in different forms. Therefore, our endotherm assignment implies also that acid sites in the small pore system are weaker than those inside the large pore system. Kermarec *et al.* (*14*) from ir study of calcined NH_4Y reached the conclusion that the weak acidic 3550 cm^{-1} hydroxyl bond in HY was associated with large pore positions and the stronger 3650 cm^{-1} found with the small pore positions. On the other hand, Eberly (*15*), Uytterhoeven *et al.* (*16*), Ward (*2, 17*) and Olson and Dempsey (*18*) all reached the opposite conclusion. Our result seems to strongly favor the latter conclusion.

ACKNOWLEDGMENTS

The author thanks Dr. F. G. Dwyer and Dr. G. H. Kühl for their valuable comments. The author also thanks the management of Mobil R & D Corporation for giving permission to publish this paper.

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