JOURNAL OF CATALYSIS 11, 342–347 (1968)

Stoichiometry of Thermochemical Transformations of NH_4Y Zeolite

JOHN CATTANACH, ELLEN L. WU, AND PAUL B. VENUTO

From the Applied Research and Development Division, Mobil Research and Development Corporation, Paulsboro, New Jersey 08066

Received March 11, 1968; revised May 20, 1968

Quantitative aspects of thermal transformations of NH_4Y have been investigated using thermogravimetric, temperature-programmed desorption, infrared, and pulsed NMR techniques. Results obtained for hydrated NH_4Y agree closely with published data. Anhydrous NH_4Y was quantitatively reconstituted from HY. Differential thermograms of ammonium ion decomposition show two distinct classes of chemisorption sites with apparent activation energies of 15 and 22 kcal/mole, respectively. The rate of dehydroxylation is apparently highly dependent on the ambient water vapor pressure. An increase in apparent activation energy from 70 kcal/mole at 10^{-2} torr to 100 kcal/mole in the presence of He shows that the reaction is probably diffusion-controlled. The N/Al atom ratio based on "chemisorbed" NH_3 is reduced from about 1.0 to 0.5 after dehydroxylation but some NH_3 is apparently more strongly held by Lewis-type sites produced. All attempts to reconstitute NH_4Y or HY from dehydroxylated zeolite Y failed.

INTRODUCTION

Significant advances have recently been made in understanding the thermal transformations (*1–6*) of NH_4Y zeolites and the application of various compositions derived therefrom in catalytic reactions (*7*). Thermogravimetric analysis of NH_4Y-type faujasites was reported in 1965 by Uytterhoeven *et al.* (*1*) and more recently by Benesi (*8*). During a study of the catalytic activity of crystalline aluminosilicates we conducted a detailed investigation of the thermochemistry of NH_4Y faujasite, including thermogravimetric, differential thermogravimetric, temperature-programmed desorption, IR, and pulsed NMR measurements. We now report these results, which confirm and significantly expand the findings of earlier workers.

EXPERIMENTAL

Materials. The parent NH_4Y-type zeolite ($\sim 2\ \mu$)—an exchanged (*6*) synthetic NaY type faujasite—had a unit cell (UC) composition (based on chemical analysis) of $(NH_4)_{45.9}(Na)_{5.1}(AlO_2)_{51}(SiO_2)_{141}(H_2O)_{199}$. Equivalent BET surface area was 676 m^2/g and samples stored over saturated $(NH_4)_2SO_4$ solution ($p/p_0 = 0.8$ at 25°C) lost 30 wt % on ignition. Matheson anhydrous NH_3 was further purified by fractional condensation and distillation *in vacuo*.

Procedures. Thermogravimetric analyses were run on a Cahn RG Electrobalance connected to a conventional gas handling and vacuum system. An ultimate vacuum of 10^{-6} torr was obtained. The sample temperature was measured by an internal thermocouple which extended down to within 5 mm of the sample bucket. In the thermogravimetric analysis (TGA), the sample (100 mg) was continuously monitored at a series of isothermal conditions. The sample weight was recorded when the rate of weight change was less than 1 μg/min.

The distribution and relative strength of NH_3 sorption sites were investigated by temperature-programmed desorption measurements. General principles underlying this technique have been reported for similar systems (*9*). Differential thermograms generated by temperature-programmed desorption *in vacuo* (DTG) were obtained with a Cahn Time Derivative Computer.

Temperature-programmed desorption (TPD) in a He stream was studied with a modified F and M model 720 gas chromatograph. The preweighed sample (50–100 mg) was held as a disc (12-mm OD) between two frits of a stainless steel reactor. This and a similar empty reactor replaced the normal analytical and reference columns. The oven control thermocouple was inserted in the outer shell of the reactor and the sample temperature was monitored by a separate thermocouple. Helium dried over freshly calcined 5A sieve was employed as the carrier gas. Samples were activated *in situ* and reconstituted by admitting a fixed partial pressure of NH_3 (*10*). Readsorption profiles and temperature-programmed desorption curves were monitored by the thermal conductivity detector. This was calibrated in the normal manner and checked against the quantity of NH_3 removed by washing the effluent stream with 100 ml of 0.1 *N* HCl solution. Honeywell-Brown (1 mV) recorders were used in all cases.

Pulsed NMR studies of pretreated catalyst samples were run at Larmor frequencies of 25 and 50 MHz. The experimental techniques and general theory underlying hydrogen determinations by this method have been reported in earlier investigations of water absorbed on silica surfaces (*11, 12*).

Infrared spectra were scanned on a Perkin-Elmer 421 dual-grating spectrometer. Samples were sprayed onto a NaCl plate and were treated *in situ* in a high-temperature cell.

RESULTS

The parent NH_4Y zeolite—equilibrated at 25°C with H_2O at 12 torr—contained about 200 mol. (molecules) H_2O/unit cell. Care was taken to eliminate subsequent hydrothermal reactions and associated intracrystalline rearrangements (*13*). Formation of the hydrogen form (HY) and loss of constitutive or chemical water produced the thermograms shown in Fig. 1A. Loss of physically sorbed H_2O and decomposition of the parent NH_4^+ ions produced a sharp maximum at 100°C and two associated shoulders at 180° and 270°C in the initial DTG curve. Infrared spectra showed a general loss of physically sorbed water prior to deamination. The NH_4^+ ions decomposed *in vacuo* below 300°C and the HY form generated was thermally stable up to 450°C. Two sharp bands developed in the IR spectra of HY at 3640 and 3545 cm^{-1}. These frequencies agree closely with those previously assigned to acidic Si–OH groups (*4, 5*) formed by the reaction of protons with specific lattice oxygens of Si–O–Al bonds.

Dehydroxylation was extremely rapid at 500°C and the weight change between 450° and 500°C corresponds to the loss of about 22 mol. H_2O/UC. In the differential thermogram, dehydroxylation produced a very sharp maximum at about 630°C corresponding to the loss of about 20 mol. H_2O/UC. The absence of any bending vibrational bands due to H_3O^+ ions in the 1650–1700 cm^{-1} region of the HY spectra showed that the water produced on dehydroxylation was derived from OH groups formerly associated with the lattice. Near complete disappearance of the 3640 and 3545 cm^{-1} bands on dehydroxylation confirmed the extensive loss of both acidic SiOH groups. Analysis (*14, 15*) of the DTG results showed an apparent first order process with an activation energy of about 70 kcal/mole of H_2O desorbed.

An apparent decrease in X-ray crystal quality occurred on dehydroxylation but this may reflect a loss of order through defect site formation rather than complete lattice collapse—production of irregular distortions in the lattice was indicated by a twofold increase in the half-peak-width at $2\theta = 54°$. Overall retention of a Y-type lattice after

TABLE 1

SORPTIVE PROPERTIES OF ZEOLITE Y SAMPLES

Sorbate	Pressure (torr)	Mol. adsorbed/UC at 25°C HY	Dehydroxylated Y
H_2O	12	199	170
Cyclohexane	20	26.9	20.2
NH_3	100	153	106
	a	(46.7)	(25.0)

[a] Quantity of NH_3 retained upon evacuation at 50°C and 10^{-5} torr.

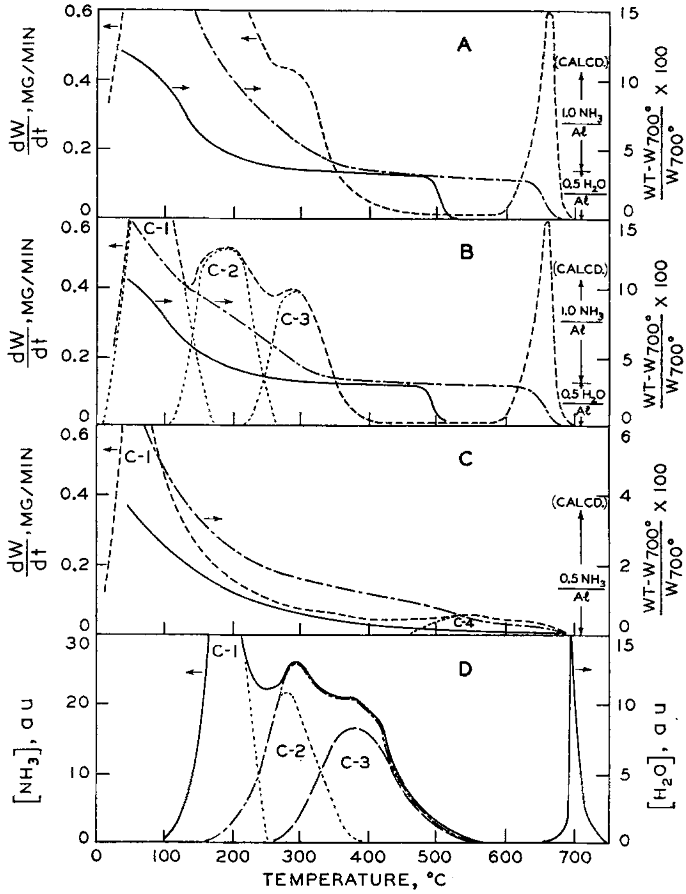

FIG. 1. (A) Dehydration and decomposition of hydrated NH_4Y. (B) Decomposition of anhydrous NH_4Y. (C) Desorption of NH_3 from dehydroxylated zeolite Y. For A, B, C: ——, isothermal thermogram; – · – programmed thermogram; – – – differential thermogram; ...... possible resolution of differential thermogram. (D) Temperature-programmed desorption of NH_3 from anhydrous NH_4Y in He. For D: ——, complete thermogram after 50°C purge; – · –, partial thermogram after 170°C purge; – – –, partial thermogram after 270°C purge; ......, profiles obtained by difference between above consecutive thermograms. Heating rate 10°C/min.

dehydroxylation was assumed from the observed cyclohexane capacity (Table 1). The dehydroxylated Y form was extremely unstable when exposed to moisture. Attempts to reconstitute NH_4Y or HY from the dehydroxylated form by reaction with H_2O at elevated temperatures or addition of NH_3 followed by H_2O at room temperature failed and generally resulted in complete loss of crystal quality and sorptive capacity. Possible reconstitution has been reported for partially dehydroxylated samples (*4*).

Anhydrous NH_4Y was reconstituted from the HY form generated at 450°C and 10^{-6} torr. Ammonia was initially admitted at 100°C to produce rapid equilibration within the small pore system, and the sample was finally equilibrated at 25°C with NH_3 at 100 torr for a period in excess of 16 hr. Total NH_3 uptake varied between 147 and 153 mol. NH_3/UC which agrees closely with values reported for complete saturation of Na faujasite (*16*) and hydrogen zeolite Y (*17*). Ammonia had presumably penetrated the sodalite units and so gained access to all available protonic sites.

Retention of about 47 mol. NH_3/UC after prolonged evacuation at 50°C and 10^{-6}

torr showed quantitative reconstitution of NH_4Y. Reformation of NH_4^+ ions was confirmed by an NH deformation band at 1445 cm^{-1} which is similar in frequency to that previously reported by other workers (*1*). A typical TGA curve (Fig. 1B) was similar to the initial thermograms and also showed complete removal of the chemisorbed NH_3 below 300°C. The criteria of chemisorption at 50°C and irreversible adsorption at elevated temperatures are somewhat arbitrary, but it may be assumed that the activation energy required is such that the resultant desorption rate is minimal.

A typical differential thermogram of NH_3 desorption from reconstituted NH_4Y is shown in Fig. 1B. The HY sample (450°, 10^{-6} torr) was initially equilibrated with NH_3 as before; and then after a preliminary evacuation (10 min), it was heated *in vacuo* at 10°C/min up to 450°C. The presence of two peaks with maxima at 66° and 177°C and an associated well-defined shoulder at about 277°C in the differential thermograms shows three distinct classes of sites for NH_3 sorption. The amount of ammonia desorbed from the weaker class of sites—designated C-1 (25°–110°C)—was dependent on the total amount of NH_3 present. It was completely eliminated by an extended evacuation at 50°C, and is attributed to "physical" sorption. Similar evacuations at elevated temperatures showed two distinct classes of chemisorption sites—hereinafter designated C-2 (110–230°) and C-3 (230–400°), with maximum rates of desorption at 180° and 280°C, respectively. Chemisorbed NH_3 formerly present at sites C-2 and C-3 (Table 2) amounted to about 30 and 21 mol. NH_3/UC, respectively, and their sum agrees reasonably well with the value of 45.9 mol. NH_3/UC calculated for decomposition of a completely reconstituted NH_4Y zeolite. The differential thermograms were reproducible, and when the temperature program was extended to 650°C, a sharp maximum corresponding to dehydroxylation was again observed at 630°C (Fig. 1B).

TABLE 2

Ammonia Loss During Temperature-Programmed Desorption in Vacuum

Temp. range (°C)	Site designation	Mol. NH_3 lost[a]/UC	
		HY	Dehydroxylated Y
25–110°	C_1	37.5[b]	28.7[b]
110–230°	C_2	29.6	11.8
230–450°	C_3	21.7	7.7
450–650°	C_4	—	6.2

[a] Within stated temperature interval.

[b] The HY and dehydroxylated Y samples (previously equilibrated at 25°C with NH_3 at 100 torr) lost 57.2 and 51.6 mol. NH_3/UC, respectively, during the preliminary evacuation.

The TGA and DTG curves for the interaction of NH_3 with the dehydroxylated form are shown in Fig. 1C. The NH_3 sorption capacity was reduced to about 106 mol. NH_3/UC. Only about 25 mol. remained after prolonged evacuation at 50°C and 10^{-6} torr, but about 5 mol. /UC were retained above 200°C by the dehydroxylated form (Table 2). A weak IR bank at 1435 cm^{-1} attributed to NH_4^+ ions disappeared at 200°C, while a band at 1610 cm^{-1} assigned to NH_3 retained by a Lewis type of interaction (*2*) persisted even above 300°C. Additional NH stretching bands at about 3340 and 3275 cm^{-1} similar to those reported (*18*) for NH_3 coordinated to surface electron-accepting sites in Cab-o-sil were also retained above 200°C. The maximum at 60°C in the differential thermogram showed that the majority of the NH_3 was "physically" sorbed. The maxima formerly associated with C-2 and C-3 were absent and NH_3 lost between 110° and 400°C was reduced to about 18.3 mol. NH_3/UC. The 6 mol. NH_3/UC lost above 450°C (Table 2) were assigned to a new class of sites, C-4.

Temperature-programmed desorption curves obtained in helium (Fig. 1D) were similar to those obtained *in vacuo* and also showed three classes of sites for NH_3 sorption in a reconstituted NH_4Y sample. Possible intracrystalline oxidation reactions previously reported (*6*) were not observed in the He stream. Almost 90 mol. NH_3/UC were retained after reconstitution and a subsequent He purge at 30°C for 10 min. The maximum desorption rates from sites C-1, C-2, and C-3 occurred at 190°, 300°, and 400°C, respectively. Ammonia was desorbed from sites C-1 and C-2 by preliminary purges at 170° and 270°C and subsequent thermograms (Fig. 1D) showed the presence of three distinct groups of sites corresponding to the loss of about 45, 27, and 18 mol. NH_3/UC. Apparent activation energies for desorption obtained by varying the heating rate from 5° to 20°C/min according to the method of Amenomiya and Cvetanovic (*9*), were about 11, 15, and 22 kcal/mole, respectively. Dehydroxylation was extremely rapid and the evolved H_2O produced a sharp peak at about 690°C (Fig. 1D). Dehydroxylation again appeared to be first order but the activation energy had increased to about 100 kcal/mole.

Values for the total hydrogen content of HY—determined by the pulsed NMR technique—were 38.6 (10 hr, 10^{-5} torr, 400°C) and 45.8 (3 hr, He, 550°C) g atoms hydrogen/UC. These values are similar to these reported by Uytterhoeven *et al.* (*1*). The total hydrogen content of dehydroxylated samples was reduced to 19.5 (3 hr, 10^{-5} torr, 600°C) and 24.4 (3 hr, He, 700°C) g atoms hydrogen/UC. These latter values considerably exceed those reported by other workers (*1*) based on deuterium exchange and thermogravimetric analysis.

DISCUSSION

Results of the present physicochemical investigation are in general self-consistent and augment the results of previous workers (*1-3*, *8*). Dehydration largely preceeds deamination when the parent NH_4Y is calcined and the HY form generated at 300° is relatively stable *in vacuo* up to 450°C. The HY form is apparently completely saturated with NH_3 during the reconstitution procedure. The activation energy of 11 kcal/mole required for subsequent desorption of "physically" sorbed NH_3 is similar to that reported for SiO_2 surfaces (*19*) and for HY at high loadings (*17*).

The N/Al atom ratio of almost unity given by the quantity of "chemisorbed" NH_3 shows that reconstitution of NH_4Y from HY previously proposed by Uytterhoeven *et al.* (*1*) may be achieved quantitatively. We have successfully prepared partially deuterated HY (DHY) from similarly reconstituted ND_3HY samples for catalytic studies (*20*).

Two distinct classes of NH_4^+ ions exist in NH_4Y which decompose with activation energies of about 15 and 22 kcal/mole, respectively. These values may only be relative due to readsorption in the He stream but they approach those reported for SiO_2/Al_2O_3 and related systems (*17*, *21*, *22*).

The wide variation in the acidic strength of HY towards NH_3 presumably relates to differences in energy of interaction which may arise at the various crystallographically discrete sites which have been proposed for other metal cations in faujasite-type structures (*23-29*). Evidence for AlO_2 units with differing environments has been reported as a result of adsorption (*27*, *28*), catalytic (*29*), ion exchange (*24*, *25*), and spectroscopic studies (*2*, *4*, *5*, *27*). The protons released on deamination are virtual point charges and the overall thermochemistry is complicated by the simultaneous reorganization of the anionic lattice. The two IR bands, assigned to acidic SiOH groups in HY (*4*, *5*), appeared simultaneously when NH_4Y was calcined, so their individual formation is apparently unrelated to the successive decomposition of NH_4^+ ions at sites C-2 and C-3. Both IR bands also disappeared rapidly as reported (*1*) on readsorption of NH_3.

The 22 mol. H_2O/UC formed during dehydroxylation corresponds to a 93% reduction of protons in HY by the elimination of almost one molecule of H_2O for every two Na free AlO_2 units. The process appeared to be first order but the reaction temperature increased from 630° *in vacuo* to 690°C in He. The apparent activation energy also increased from about 70 kcal/mole to almost 100 kcal/mole. The rate of dehydroxylation of HY is highly dependent on the ambient water vapor pressure, which was about 10^{-2} torr during the vacuum calcination. A similar dependency has been reported in the dehydroxylation of clays, notably kaolinite (*5*, *30*).

The N/Al atom ratio based on the quantity of "chemisorbed" NH_3 was reduced after dehydroxylation from about 1.0 to 0.5. This is consistent with the formation of one new electron-deficient site from every two former protonic sites, as indicated in the mechanism reported by Uytterhoeven *et al.* (*1*). Ammonia is apparently retained by a Lewis-type of interaction which gives rise to a class of stronger sorption sites, designated C-4. Irreversible sorption of other molecules has been reported after dehydroxylation (*4*) and the latter type of interaction is consistent with the more active sites reported for SiO_2/Al_2O_3 and Al_2O_3 surfaces (*21*, *22*). The use of NH_3 for probing the acidity of zeolite surfaces is complicated because of its high reactivity and penetration of the small pore system which is inaccessible to reactant molecules (*24*, *25*).

The total hydrogen contents of samples calcined *in vacuo* at 400°C or in He at 550°C—38.6 and 45.8 g atoms hydrogen/UC, respectively—agree closely with that based on the number of Na^+-free AlO_2 units in HY, namely 45.9/UC. The lower hydrogen content of samples calcined above 600° is consistent with dehydroxylation but the reduction observed is much less than predicted by the thermogravimetric results. Terminal OH groups on the 2-μ crystallites may account for about 0.5 g atoms hydrogen/UC (*31*). Incomplete desorption may have induced a partial rearrangement of chemical water as reported by Kerr (*13*). The values obtained, however, are presumably more analogous to the normal type of calcinations employed in catalytic studies.

ACKNOWLEDGMENTS

We wish to thank Dr. D. Woessner and Dr. J. Zimmerman of the Mobil Field Research Laboratory, Dallas, Texas, for running the pulsed NMR analyses, and Dr. G. T. Kerr of Mobil and Professor L. S. Bartell of the University of Michigan for very helpful discussions.

REFERENCES

1. UYTTERHOEVEN, J. B., CHRISTNER, L. G., AND HALL, W. K., *J. Phys. Chem.* **69**, 2117 (1965).
2. ANGELL, C. L., AND SCHAFFER, P. C., *J. Phys. Chem.* **69**, 3463 (1965).
3. STAMIRES, D. N., AND TURKEVICH, J., *J. Am. Chem. Soc.* **86**, 749 (1964).
4. LIENGME, B. V., AND HALL, W. K., *Trans. Faraday Soc.* **62**, 3229 (1966).
5. WHITE, J. L., JELLI, A. N., ANDRÉ, J. M., AND FRIPIAT, J. J., *Trans. Faraday Soc.* **63**, 461 (1967).
6. VENUTO, P. B., WU, E. L., AND CATTANACH, J., *Anal. Chem.* **38**, 1266 (1966).
7. VENUTO, P. B., AND LANDIS, P. S., *Advan. Catalysis* **18**, 259 (1968).
8. BENESI, H. A., *J. Catalysis* **8**, 368 (1967).
9. AMENOMIYA, Y., AND CVETANOVIC, R. J., *J. Phys. Chem.* **67**, 144 (1963).
10. BEEBE, R. A., EVANS, P. L., KLEINSTEUBER, T. C. W., AND RICHARDS, L. W., *J. Phys. Chem.* **70**, 1009 (1966).
11. ZIMMERMAN, J. R., HOLMES, B. G., AND LASATER, J. A., *J. Phys. Chem.* **60**, 1157 (1956).
12. WOESSNER, D. E., AND ZIMMERMAN, J. R., *J. Phys. Chem.* **67**, 1590 (1963).
13. KERR, G. T., *J. Phys. Chem.* **71**, 4155 (1967).
14. FREEMAN, E. S., AND CARROLL, B., *J. Phys. Chem.* **62**, 394 (1958).
15. HOROWITZ, H. H., AND METZGER, G., *Anal. Chem.* **35**, 1464 (1963).
16. BARRER, R. M., AND GIBBONS, R. M., *Trans. Faraday Soc.* **59**, 2569 (1963).
17. BENSON, J. E., USHIBA, K., AND BOUDART, M., *J. Catalysis* **9**, 91 (1967).
18. CANT, N. W., AND LITTLE, L. H., *Can. J. Chem.* **43**, 1252 (1965).
19. STONE, F. S., AND WHALLEY, L., *J. Catalysis* **8**, 173 (1967).
20. VENUTO, P. B., WU, E. L., AND CATTANACH, J., *Soc. Chem. Ind., Conf. Mol. Sieves., London, 1967*, to be published as a "Molecular Sieve Monograph."
21. KEVORKIAN, V., AND STEINER, R. O., *J. Phys. Chem.* **67**, 545 (1963).
22. HIRSCHLER, A. E., *J. Catalysis* **6**, 1 (1966).
23. BROUSSARD, L., AND SHOEMAKER, D. P., *J. Am. Chem. Soc.* **82**, 1041 (1960).
24. BARRER, R. M., *Endeavour* **23**, 122 (1964).
25. BRECK, D. W., *J. Chem. Educ.* **41**, 678 (1964).
26. BAUR, W. H., *Am. Mineralogist* **49**, 697 (1964).
27. YATES, D. J. C., *J. Phys. Chem.* **70**, 3693 (1966).
28. HABGOOD, H. W., *Can. J. Chem.* **42**, 2340 (1964).
29. TURKEVICH, J., NOZAKI, F., AND STAMIRES, D., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam* **1**, 714 (1964) (Wiley, New York, 1965).
30. BRINDLEY, G. W., SHARP, J. H., PATTERSON, J. H., AND NARAHARI, B. N., *Am. Mineralogist* **52**, 201 (1967).
31. KERR, G. T., DEMPSEY, E., AND MIKOVSKY, R. J., *J. Phys. Chem.* **69**, 4050 (1965).