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Synthetic Offretite

II. Decomposition of Organic Cations and Generation of Acidity

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The organic transformations and associated structural changes during thermal decomposition of a tetramethylammonium (TMA) offretite have been investigated. In the aluminosilicate structure, lattice associated hydroxyl groups, confirmed as protonic in nature by interaction with NH_3, were generated from TMA cations, an unusual proton precursor. Dehydroxylation of acid offretite at approximately 500°C occurred to give electron acceptor (Lewis) sites which coordinated with NH_3. A complex mixture of coke, trimethylamine, and twenty-one low molecular weight molecules, including methanol, carbon monoxide, methyl ether, C_2–C_4 olefins, and hydrogen can be formed from vacuum fragmentation of the bulky TMA cations within the narrow offretite channels. A mechanistic interpretation, which includes superimposition of many "classical" reaction patterns rationalizes the observed product distributions.

INTRODUCTION

We recently reported the physicochemical, thermal, crystallographic, and morphological properties of a synthetic offretite (*1*). Tetramethylammonium (TMA) cations retained by the zeolite during crystallization are associated with a portion of the anionic sites in this offretite. These bulky organic cations (diameter 6.94 Å) appear to be located in the large intracrystalline pores along the *c*-crystallographic axis, where they effectively hinder adsorption of hydrocarbon sorbates. Upon thermal fragmentation of these species, the capacity of the aluminosilicate for sorption of *n*-hexane and cyclohexane increases enormously.

In the present paper we report results of a study on the organic transformations of the alkylammonium cations and the associated lattice structural changes that occur during the thermal decomposition of the TMA offretite. A role for the TMA cations as proton precursors is indicated.

EXPERIMENTAL

Materials

The sample of synthetic offretite used in the present study was of high crystallinity (X-ray) and had the following composition: $[(CH_3)_4N]_{0.33} \cdot Na_{0.18} \cdot K_{0.64} \cdot (AlO_2)_{1.00} \cdot (SiO_2)_{4.29}$ based on actual chemical analyses. The cationic excess may be attributed to either $(CH_3)_4NOH$ or alkali occluded in the zeolitic pores during synthesis. After air calcination at 483°C, the zeolite sorbed 16.2 wt % H_2O, 8.3 wt % *n*-hexane, and 5.9 wt % cyclohexane, and had a BET surface area (N_2) of 427 m^2/g.

The NH_3 (Matheson anhydrous) was purified by trap-to-trap distillation, condensation, and evacuation.

APPARATUS AND PROCEDURES

(A) *Observation of Zeolitic Transformations*

A high temperature infrared cell (Fig. 1) in which *in situ* evacuation, calcination,

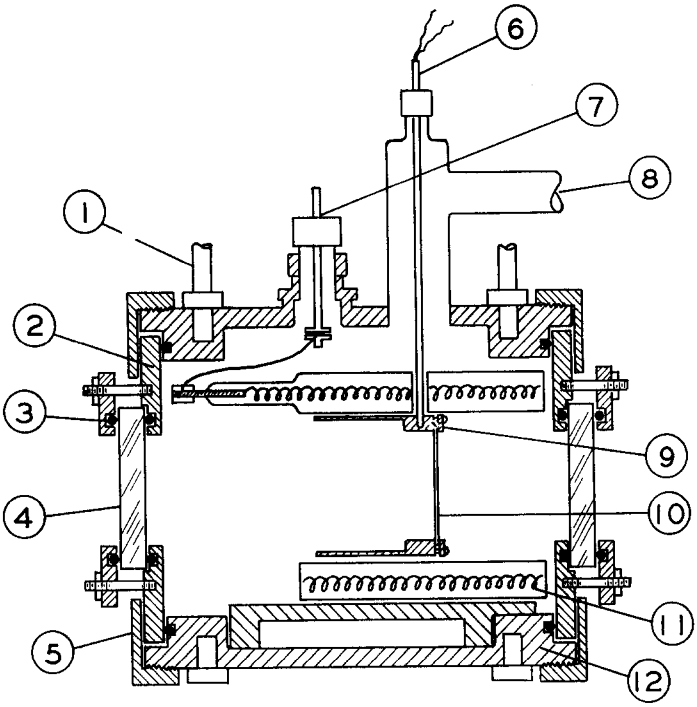

FIG. 1. High temperature infrared cell: (1) water inlet for cooling; (2) stainless steel window holder; (3) "O" ring; (4) NaCl window; (5) brass end cap; (6) Iron Constantan thermocouple; (7) vacuum feed-thru; (8) connection to vacuum system; (9) stainless steel sample holder; (10) zeolite sample; (11) quartz resistance heater; and (12) stainless steel cell body.

and ammonia sorption on the zeolite could be performed together with simultaneous observation of its infrared spectrum, was employed. The cell was connected to a conventional gas handling and vacuum system capable of maintaining pressure in the 10^{-6} Torr range.

Infrared spectra were recorded on a Perkin-Elmer 421 grating spectrophotometer, modified by the addition of a presample chopper to eliminate the effect of spurious radiation originating from the heater and hot sample. A wider than normal slit had to be used due to the reduction of source intensity by the presample chopper and low transmission of the sample. Spectral resolution was 4 cm^{-1} at 3600 cm^{-1} and 2 cm^{-1} at 1600 cm^{-1}. A similar but unheated cell was placed in the reference beam for compensation.

Small particle size ($\sim 0.2\ \mu \times 1\ \mu$) offretite, fractionated by sedimentation in water, was used to minimize scattering of ir radiation. Stepwise (25°C increments) heating of the sample was employed to effect TMA decomposition, dehydroxylation, and desorption of adsorbed ammonia.

(B) *Characterization of Gaseous Decomposition Products*

Two gram samples of TMA-offretite were vacuum calcined in a tubular Vycor reactor connected to a conventional vacuum and gas handling system. Condensable gaseous products were isolated by three traps maintained at liquid N_2 temperature; noncondensables were allowed to expand into an evacuated bulb. The condensables were further separated into −81°C (dry-ice acetone trap) and −196°C (liquid N_2 trap) fractions.

Each of the gaseous fractions was transferred via the gas handling system to a 10 cm KBr ir cell and scanned on the Perkin-Elmer 421 Spectrophotometer. The components were identified by comparison with known spectra, matching rotational fine structure of ir bands. The products were subsequently analyzed on a Consolidated Electrodynamics Corporation Model 21–104 Mass Spectrometer using an ionization voltage of 10 eV. Data are shown in Table 1.

TABLE 1
DECOMPOSITION PRODUCTS FROM TMA CATIONS IN OFFRETITE[a]

	Distribution (estimated mole %)[b,c]		
Products	85–275°C	275–425°C	Total
$(CH_3)_3N$	69	35	46
H_2	1	22	15
CH_3OH	16	7	9
CO	2	12	9
$(CH_3)_2O$	3	9	7
CO_2	6	5	5
CH_4	<1	7	5
C_2H_4	—	1	1
C_3H_6	—	1	1
H_2O	<1	1	1
Trace Products[d]			
NH_3, C_2H_6, C_3H_8, C_4H_8, C_4H_{10}, NO, $HC{\equiv}CH$ ($CH_3C{\equiv}N$, $HC{\equiv}N$, $CH_2{=}CH{-}CH{=}CH_2$, N_2H_4)			

[a] Calcination (*in vacuo*): 16 hr at 85°C, then 3½ hr to 275°C, hold for 2 hr, then 1 hr to 450°C, and hold for 4 hr. The choice of 275°C as the upper limit for decomposition over the lower temperature range was arbitrary.

[b] Estimation based on relative pressure of condensable and noncondensable fractions and mass spectral analyses.

[c] Supporting identifications were furnished by NMR and gas chromatographic techniques.

[d] Characterized by mass spec. only, except for NH_3. Products in parentheses were found in trace amounts when sample was calcined directly to 425°C (without stopping at 275°C).

RESULTS

Decomposition of Tetramethylammonium Cations

Pertinent regions of the infrared spectra of synthetic TMA offretite after evacuation at various temperatures are compared in Fig. 2. All bands due to the TMA ion decreased drastically in intensity above 300°C, reflecting rapid decomposition of the quaternary cation. (The maximum rate of decomposition in N_2 atmosphere occurred at 410°C (*1*), according to differential thermal analysis.) Concomittantly, new bands appeared at 3690, 3600, and 3550 cm^{-1} in the OH stretching region. (The band at 3735 cm^{-1} is associated with surface silanol groups.) These bands are not likely to be due to adsorbed water because they occurred in vacuum where readsorption of water was minimized. Therefore, the data showed clearly that OH groups were generated as a direct consequence of the TMA ion decomposition.

Methoxy Intermediate

After extensive TMA cation decomposition (400°C), an intensity change was observed in ν_{CH} region (Fig. 2). The shoulder at about 2950 cm^{-1}, initially appearing on the side of the 2930 cm^{-1} band, gained in intensity as the latter decreased. The intensity of the 2860 cm^{-1} band appeared to decrease less, relative to that of the 2930 cm^{-1} band. These observed changes may indicate the formation of a new surface methoxy species, CH_3–O–Zeol (I). However, these methoxy species apparently are not stable at 425°C but undergo further decomposition. Surface methoxy groups on silica and alumina have been reported to give characteristic ir bands at 2959 and 2855 cm^{-1} (*2*) and 2950 and 2840 cm^{-1} (*3*), respectively.

Protonic Acidity

The three ν_{OH} bands, from TMA decomposition, shifted somewhat to 3690, 3615, and 3550 cm^{-1} after cooling to 100°C (Fig. 3a). (Mobility of the hydrogen has been proposed (*4*) to explain the lower frequency observed in aluminosilicate hydroxyls at high temperature.) The protonic nature of the hydrogen on these OH groups was confirmed by their interaction with ammonia to give NH_4^+ ions, as evidenced by the characteristic ir bands (Fig. 3b–d). As ammonia coverage increased, the broad $\delta_{NH_4^+}$ band at about 1415 cm^{-1} decreased and was replaced by a sharp band at 1465 cm^{-1}. This suggests a more significant

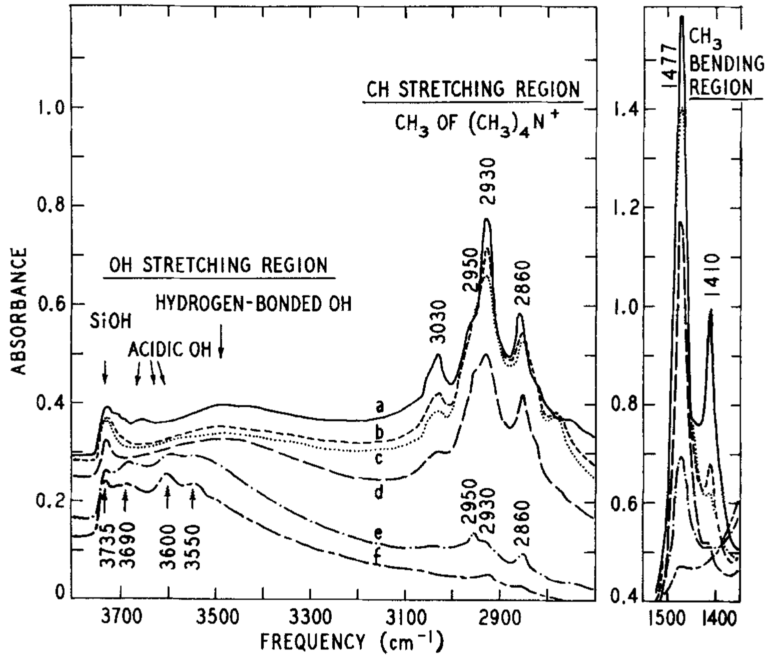

FIG. 2. Changes in infrared spectrum of offretite (self-supporting wafer, pressed under 20 000 lb/in^2, 10 mg/cm^2 "thickness"). Vacuum calcined and scanned *in situ* at: (a) 100; (b) 200; (c) 300; (d) 350; (e) 400; and (f) 425°C. Curves (e) and (f) were displaced for purpose of display.

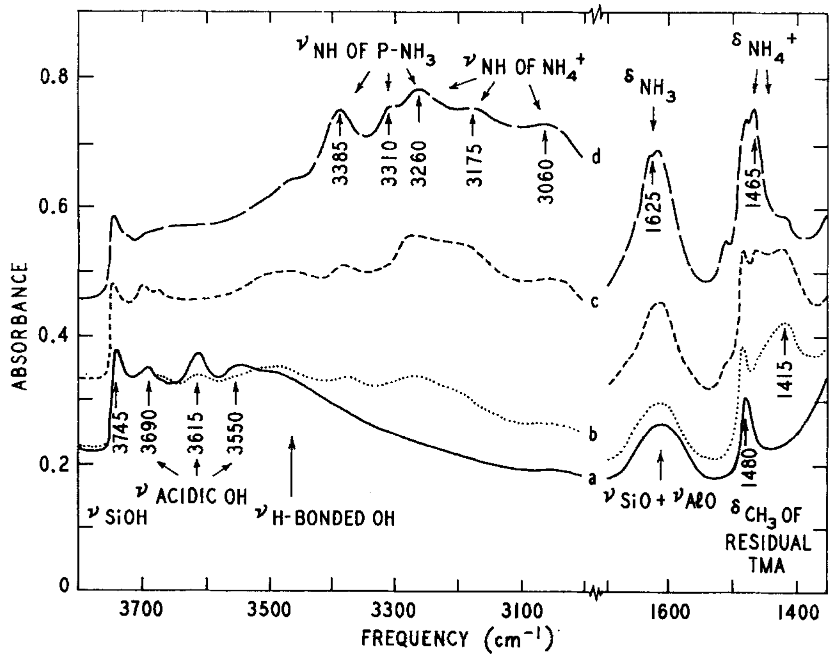

FIG. 3. Infrared spectra of H-offretite before and after NH_3 adsorption. Spectra scanned at 100°C after (a) vacuum calcined at 425°C; (b) exposed to NH_3, at 100°C, $P = 3.4 \times 10^{-3}$ Torr; (c) $P = 2.15 \times 10^{-2}$ Torr; and (d) $P = 0.98$ Torr. P-NH_3 stands for physically-sorbed NH_3. Curve (c) and (d) displaced for purpose of display.

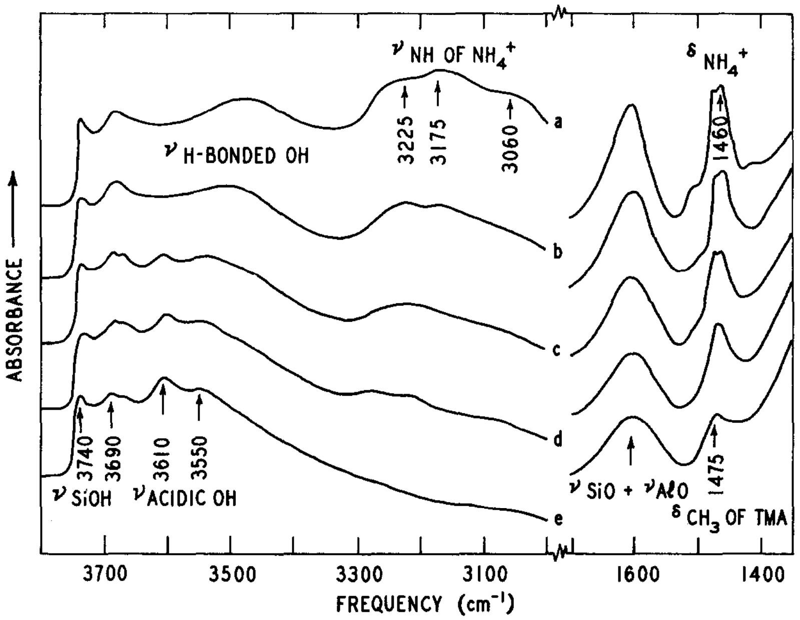

FIG. 4. Infrared spectra of NH_3-treated offretite at various stages of desorption. Spectra scanned after NH_3 desorption at: (a) 100; (b) 200; (c) 250; (d) 300; and (e) 350°C. Curves displaced for purpose of display.

change in the NH_4^+ ion environment than mere H-bonding to physically-sorbed ammonia.

The strengths of the three kinds of OH groups differed. Hydroxyl groups at 3690 cm^{-1} showed a rather weak interaction toward ammonia; they were removed only at high ammonia coverage (Fig. 3d) but regenerated by 100°C evacuation (Fig. 4a). The other acid OH groups reacted more strongly with ammonia, as shown by persistence of NH_4^+ ions after evacuation at 300°C (Fig. 4d). Complete regeneration of the H-offretite required an overnight evacuation at 350°C (Fig. 4e).

Dehydroxylation

Decrease in the intensity of these acidic OH bands with further calcination is clearly shown in Fig. 5, whereas the terminal silanol groups were only slightly affected. Complete dehydroxylation was achieved by evacuation at 600°C. A sharp endothermic peak was observed at about 560°C on the DTA profile of offretite (*1*), indicative of this structural transformation.

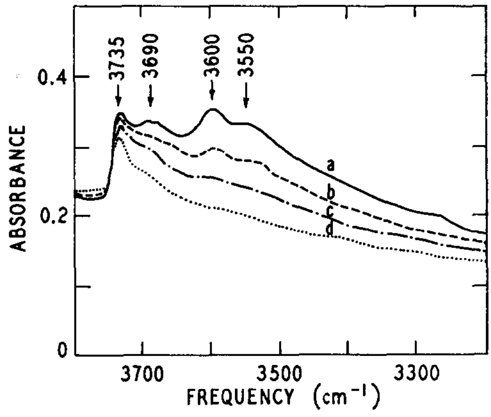

FIG. 5. Changes in infrared spectrum (ν_{OH} region) of offretite during dehydroxylation. Spectra scanned after evacuated at: (a) 425; (b) 500; (c) 550; and (d) 600°C.

Lewis Acidity

No observable acidic OH groups remained after dehydroxylation (Fig. 6a). Upon exposure to ammonia (Fig. 6b), ir bands characteristic of ammonia coordinated to electron-accepting sites were produced. This implies that Lewis acid sites were generated by dehydroxylation. At

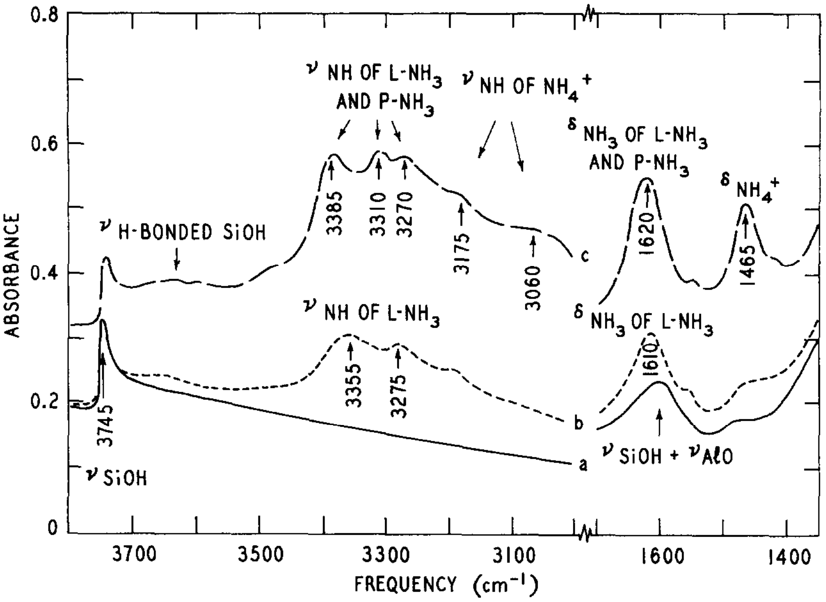

FIG. 6. Infrared spectra of dehydroxylated offretite before and after NH_3 adsorption. Spectra scanned at 100°C after: (a) vacuum calcined at 600°C; (b) exposed to NH_3, at 100°C, $P = 0.16$ Torr; and (c) $P = 1.3$ Torr. L-NH_3 stands for NH_3 coordinated to Lewis acid sites and P-NH_3 for physically-sorbed NH_3. Curve (c) displaced for purpose of display.

higher ammonia coverage, some absorption attributable to NH_4^+ ions was also observed. These probably formed on a few residual acidic OH groups (Fig. 6c).

Desorption of the ammonia sorbed via coordination on the surface was carried out to probe the strength of the Lewis acid sites. Removal of ammonia from these was achieved by evacuation at 300°C (Fig. 7).

Decomposition Products

Twenty-one gaseous products obtained from vacuum calcination of a large size, fixed bed TMA-offretite catalyst have been identified. Note that the activation program for the large size sample (Table 1, footnote a) differs from that of the self-supporting water in the ir cell. The product distribution has been analyzed as a function of decomposition temperatures (Table 1). Decomposition of solid TMA hydroxide has been reported to occur at 135–140°C (*5*). Therefore, we would expect products from any occluded TMA hydroxide in offretite to be included in the lower temperature fraction of the decomposition (85–275°C). Thirty-one percent of the total product was found in this portion.

Trimethylamine accounted for nearly half of the products. Hydrogen was next in abundance. In addition, oxygenated compounds, hydrocarbons, and traces of other nitrogen compounds were found. The decomposition in the absence of air left a dark gray organic residue (1.8% carbon and <0.1% nitrogen) on the surface of the offretite.

DISCUSSION

Nature of Acidity on Offretite

The ir data, showing the generation of three distinct ν_{OH} bands (at 3690, 3615, and 3550 cm^{-1}) from decomposition of the TMA cations (Fig. 2), and disappearance of those bands with admission of ammonia to the offretite sample (Fig. 3), confirm the presence of lattice-associated acidic OH groups. The role of TMA cations as proton precursors in offretite is clearly demonstrated.

The lattice-associated OH groups re-

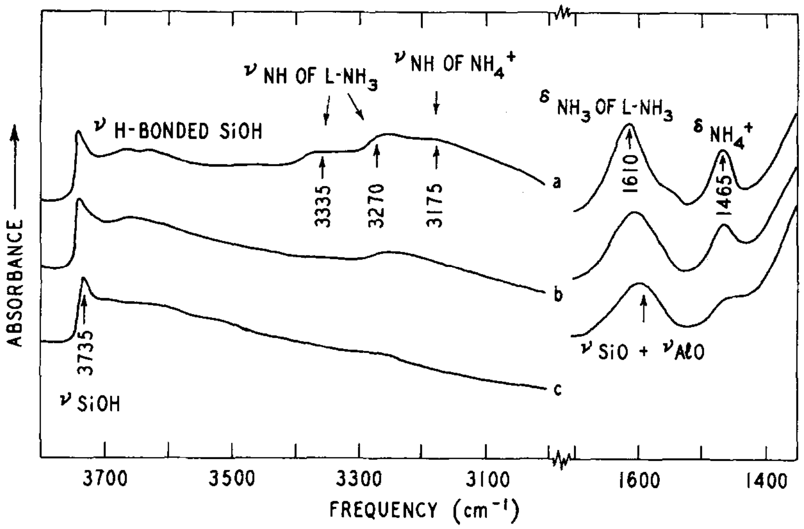

Fig. 7. Infrared spectra of NH_3-treated dehydroxylated offretite at various stages of desorption. Spectra scanned after NH_3 desorption at: (a) 100; (b) 200; and (c) 300°C. L-NH_3 stands for NH_3 coordinated to Lewis acid sites. Curves displaced for purpose of display.

sulted from protons interacting with specific lattice oxygens of Si–O–Al bonds, analogous to hydroxyl formation in HY zeolite (*6*). The latter exhibits only two bands at about 3650 and 3550 cm^{-1} (*7–11*), without a higher frequency band as in the case of offretite.

Differences in the ir absorption frequencies of these OH groups reflect dissimilarities in their environments. For example, in HY zeolite, the high and low frequency bands have been associated with hexagonal prism oxygen bridging two adjacent cubo-octahedra and oxygen on six member rings in the hexagonal prism, respectively (*8, 10–12*). There are six crystallographically different oxygens in the framework of offretite (Fig. 8). The protons released from TMA cation decomposition could interact with three different kinds of oxygens in the lattice to give rise to three distinct OH species. However, it is not possible to specify the precise location of these different OH groups at present.

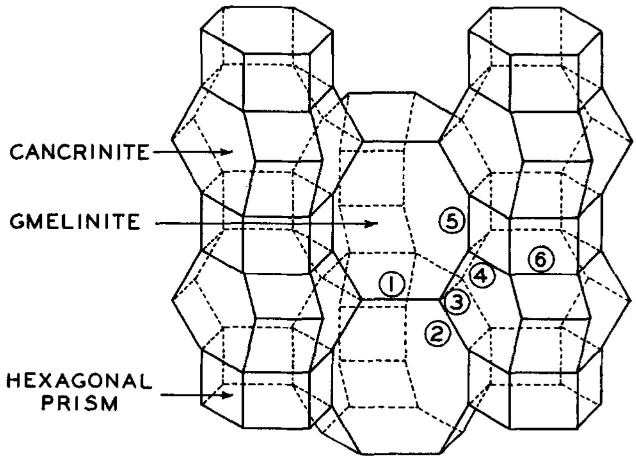

Fig. 8. Line drawing of cage system in offretite. An oxygen is situated at midpoint of each line segment; an Si or Al atom at each vertex. Six crystallographically different oxygens are indicated.

Nearness of other cations (Na^+ and K^+), location of the hydroxyl oxygens in the offretite lattice, as well as other environmental differences, can affect the frequency and acidic strength of these OH groups. Such variation in strength has been revealed by differences in their retention of ammonia (Fig. 4). In comparison, complete removal of chemisorbed ammonia from NH_4Y can be achieved by evacuation at 300°C (*7*). But some sites on offretite still retain their sorbed ammonia after similar treatment. Thus, the H-offretite generated from thermal decomposition of TMA offretite possesses a population of acid sites somewhat stronger than those in HY zeolite.

The acidic OH groups in offretite, though generated from a different precursor (TMA cations) than those in the NH_4–HY system, undergo dehydroxylation at about the same temperature, 500°C (*7*). Generation of Lewis acidity from dehydroxylation on offretite may proceed via a mechanism similar to that postulated for HY (*6, 13, 14*), with elimination of one molecule of water from two acidic OH groups. The interaction of ammonia with the Lewis acid sites on offretite is weaker than that in dehydroxylated Y zeolite. No detectable ammonia remained on offretite after desorption at 400°C, whereas in Y-zeolite, some resisted evacuation at 500°C (*7*).

Tetramethylammonium Cation Decomposition Pathways

A reasonable mechanistic interpretation of the fate of the organic cations must not only be consistent with the extremely complex product distribution (Table 1), but also with the clearly associated generation of protonic acid sites. Some possible reaction pathways are postulated in Table 2, a superimposition of which can explain the formation of most of the products. Some of these reaction pathways have been discussed in detail (*23*) in a different system—tetramethylammonium Y-zeolite.

The decomposition rate of TMA cations in offretite (under vacuum) became significant above 300°C and was complete by 425°C, according to the ir observations. The protons could conceivably be formed from any one of the proton generating schemes in Table 2. However, due to the relatively anhydrous environment, a mechanism similar to Scheme L is more probable.

In the case of the large, fixed-bed sample, a hydroxylic sorbate pool can be present in the intracrystalline voids, probably deriving from water physically sorbed at the lower temperatures, water of hydration of the cations, or, at the higher temperatures, water of constitution (Scheme F).

Methane is the only hydrocarbon which

TABLE 2

Postulated Reaction Pathways in Decomposition of TMA Cations in Offretite[a]

Scheme	Reaction pathway	Expected products
A	Nucleophilic attack of H_2O on methyl of TMA cations (*18*)	$(CH_3)_3N$, CH_3OH, HO–Zeol
B	Nucleophilic attack of CH_3OH on methyl of TMA cations (*18*)	$(CH_3)_3N$, $(CH_3)_2O$, HO–Zeol
C	Pyrolysis of occluded TMA hydroxide (*5*)	$(CH_3)_3N$, CH_3OH, $(CH_3)_2O$, H_2O
D	Collapse of TMA cation to form surface methoxy species (I)	$(CH_3)_3N$, CH_3–O–Zeol (I)
E	Pyrolysis of $(CH_3)_3N$ (*19*)	C_2H_4, NH_3, $HC{\equiv}CH$, $HC{\equiv}N$, $CH_3C{\equiv}N$
F	Dehydroxylation of HO–Zeol	H_2O, $\bar{O}$–Zeol $\cdots$ $^+$–Zeol
G	Hydride transfer from CH_3OH to species I	CH_4, HCHO (II), HO–Zeol
H	Hydride transfer between two species I	CH_4, HCHO (II), $\bar{O}$–Zeol $\cdots$ $^+$–Zeol
J	Decomposition of formaldehyde or related intermediate (II)	H_2, CO
K	Water gas shift reaction between H_2O and CO (*17*)	H_2, CO_2
L	Ylide or carbene mechanism (*20–22*)	C_2 to C_4 olefin, NH_3, HO–Zeol

[a] Literature citations refer to reports on the indicated reaction in nonzeolitic systems.

was produced in significant amounts in TMA decomposition. It can be formed via intramolecular hydride-transfer reaction, Schemes G and H, involving a surface methoxy species (CH_3–O–Zeol, I), whose formation (Scheme D) is supported by the ir data cited above and material balance after 85–275°C decomposition (Table 1). Similar methoxy species have been postulated as intermediates in the dehydration of methanol over alumina and silica-alumina catalysts (*15*). Hydride transfer involving methanol or hydride donor has also been reported (*16*). The operation of Scheme H would depend on many geometric factors such as the distance between intrazeolitic AlO_4-sites and the pore-channel configuration. The suggested zeolite structure with cation-anion pair defects (Scheme H) is analogous to that remaining after dehydroxylation (Scheme F) (*6, 13, 14*).

Hydrogen, the product second in abundance, and carbon monoxide can result (Scheme J) from decomposition of formaldehyde (II) or a closely related (dehydrogenated) species as depicted in Schemes G and H. Although Scheme J predicts equal abundance of hydrogen and carbon monoxide, considerably more hydrogen was found in the decomposition at 275–425°C (Table 1). Some carbon monoxide can undergo the water gas shift reaction, for which the thermodynamics are quite favorable at 300–450°C (*17*), to produce carbon dioxide and more hydrogen (Scheme K).

CONCLUSIONS

The role of TMA cations as proton precursors in synthetic offretite has been demonstrated. Thermal fragmentation of the quaternary ammonium cations results in formation of lattice-associated hydroxyl groups, with infrared absorption frequencies similar to those found on the hydrogen form of Y-type faujasite. The H-offretite so generated possesses a population of acid sites stronger than those in HY. Formation of the complex mixture of twenty-one organic reaction products in the fixed-bed reactor can be explained by superimposition of a number of reaction pathways for which precedents have been established in classical organic chemistry or nonzeolitic catalyst systems. A surface methoxy intermediate may play an important role in these transformations.

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