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A. J. Moffat
M. M. Johnson
Alfred Clark

Phillips Petroleum Company,
Bartlesville, Oklahoma 74003

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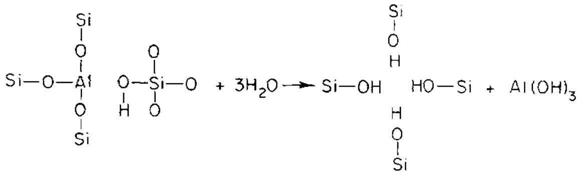
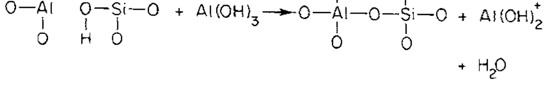
Thermal Decomposition of Ammonium Y Zeolite

Products formed by the thermal decomposition of ammonium Y zeolite have recently been discussed (*1–4*). By calcining at 500°C in shallow and deep beds, or by using calcination conditions such that the decomposition product gases remain in the vicinity of the zeolite, different products were obtained. The products have been distinguished by their hydrothermal stabilities, thermograms, reactivity to ammonia, ion-exchange and adsorptive capacities, silica to alumina ratios, and by differential thermal analysis (*1–4*).

Kerr (*2*) has suggested a mechanism for the stabilization process in which tetrahedrally coordinated aluminum ions are split out of the zeolite lattice and new Si–O–Si bonds are formed. It was concluded from thermogravimetric studies that the final form of the zeolite after calcination for 2–4 hr at 700–800°C contained no chemical water. The suggested mechanism is:



$$\mathrm{Si{-}O{-}\underset{\underset{Si}{|}}{\underset{O}{\underset{|}{\overset{\overset{\overset{Si}{|}}{O}}{\overset{|}{Al}}}}}\quad \underset{H}{\underset{|}{O}}{-}\underset{O}{\underset{|}{\overset{\overset{O}{|}}{Si}}}{-}O + 3H_2O \longrightarrow Si{-}OH\quad \underset{\underset{\underset{Si}{|}}{O}}{\overset{\overset{\overset{Si}{|}}{O}}{\overset{H}{}}}\;\; HO{-}Si + Al(OH)_3} \qquad (1)$$



$$\mathrm{O{-}\underset{O}{\underset{|}{\overset{\overset{O}{|}}{Al}}}\quad \underset{H}{\underset{|}{O}}{-}\underset{O}{\underset{|}{\overset{\overset{O}{|}}{Si}}}{-}O + Al(OH)_3 \longrightarrow O{-}\underset{O}{\underset{|}{\overset{\overset{O}{|}}{Al}}}{-}O{-}\underset{O}{\underset{|}{\overset{\overset{O}{|}}{Si}}}{-}O + Al(OH)_2^+ + H_2O} \qquad (2)$$

The four SiOH groups were believed to condense to form Si–O–Si bonds and water.

However, Kerr (*1*) has reported that after calcination at 500°C, the stabilized zeolite still contains about half as much chemical water as hydrogen Y zeolite. This chemical water could be present in the form of –SiOH or –AlOH groups.

In order to study the structural surface groups on Y zeolites, the decomposition of ammonium Y zeolite has been studied using thermal analysis, infrared spectroscopy, ion-exchange and X-ray diffraction. For comparison with the ultrastable zeolite, an ammonium Y zeolite stabilized by multivalent cations (magnesium) was studied. The zeolite composition has previously been shown to be hydrothermally stable up to high temperatures in contrast to ammonium and sodium ammonium Y zeolites.

Ammonium Y was prepared and decomposed by Procedure A of McDaniel and Maher (*3*) except that the second calcination was made at 600, 700, and 815°C. Ammonium Y was also calcined in a flowing steam atmosphere (2 psig) at 500 and 650°C by the procedure of Hansford (*6*). Samples were also prepared by thermal decomposition of ammonium Y zeolite under conditions such that the off gases were contained in the vicinity of the zeolite. Various calcination temperatures between 500 and 600°C were used. Thermogravimetric analyses in flowing helium of the above samples were similar to the "deep bed" sample of Kerr (*1*), i.e., no abrupt weight loss near 600°C was observed. Similarly, no abrupt temperature change near 600°C was observed by differential thermal analysis. The samples had lattice parameters, a_0, in the range 24.51 to 24.41 Å, surface areas of 880 to 750 m^2 g^{-1}, and crystallinities of 70 to 90% relative to a standard NaY sample. These results indicate that all samples are similar, at least in gross properties, to the "deep bed" samples of Kerr (*1*). Rehydration followed by calcination also indicated that the samples were of the "ultrastable" type since little decay of the crystal structure or adsorption capacity was observed. Furthermore, depending on the sample, the ion-exchange capacity, as determined by treatment with 10% sodium nitrate solution at 70°C, was only 45–50% of that of the original ammonium Y zeolite. However, the exchange capacity was greater when exchange solutions of higher pH were used.

Thermal analyses, hydrothermal stabilities, surface areas, and crystallinities of magnesium hydrogen Y zeolites (*5*) are similar to those of the "ultrastable" zeolites. Since magnesium hydrogen Y zeolite has a large population of hydroxyl groups similar to hydrogen Y, infrared studies have been made to examine the existence and nature of hydroxyl groups on ultrastable zeolites.

The decomposition of ammonium Y zeolite was carried out, for reference, under conditions similar to the "shallow bed" of Kerr (*1*). Ammonium Y in the form of pressed wafer (0.05 g, 1-in. diam) was also decomposed under vacuum and in flowing helium. Products were the normal hydrogen Y as shown by thermal analysis, X-ray diffraction, adsorption capacity, and exchange properties. The characteristic infrared spectrum is shown in Fig. 1a. The spectra of hydrogen Y and magnesium hydrogen Y have been discussed previously (*5, 7, 8*). Results for the two materials were equivalent after calcination up to 500°C. However, after calcination above about 550°C, distinct differences were observed in the spectra of the two zeolites. In the case of the NH_4Y, there is a sudden increase in intensity of the 3740 cm^{-1} band and a rapid decrease in the 3650 and 3550 cm^{-1} band intensities suggesting loss of crystal structure and the formation of an amorphous material. In the case of magnesium stabilized zeolite, these changes are not observed apart from the intensity decrease of the 3650 cm^{-1} band (*5*). The spectral changes occur close to the temperatures at which changes are observed in the thermal analyses.

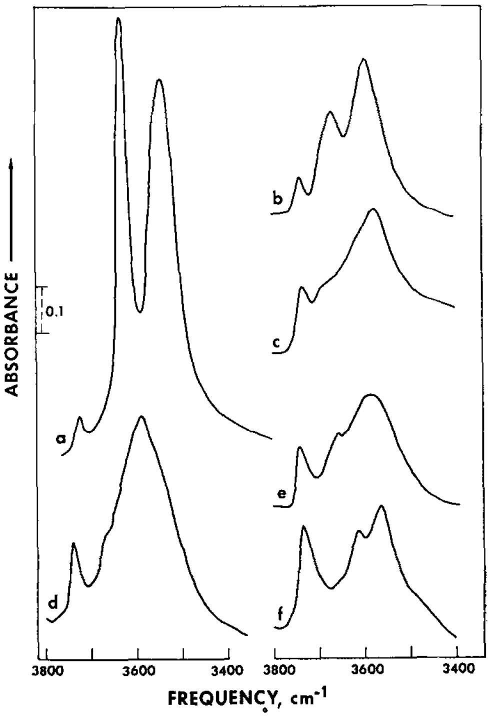


FIG. 1. Spectra of hydrogen Y zeolites after calcination at 500°C: (a) simple evacuation; (b) steamed at 500°C [Ref. (*6*)]; (c) steamed at 650° [Ref. (*6*)]; (d) calcined by procedure of Ref. (*3*), final calcination 600°C; (e) as (d) but calcination at 700°C; (f) as (d) but calcination at 815°C.

The spectra of the ultrastable zeolites are completely different from the above two zeolites. Typical spectra are shown in Fig. 1 and compared with hydrogen Y zeolite. All samples were recalcined at 500° C. As shown, the intensities of the hydroxyl groups are greatly decreased compared to those of hydrogen Y. Probably more significant is the change in frequencies and relative intensities of the hydroxyl bands. In all cases, hydroxyl groups are observed. Thus, in contrast to the conclusions reached from thermogravimetric studies (*2*), after calcination at 815°C, chemical water, in the form of structural hydroxyl groups, is detected by infrared spectroscopy. The greater concentration of hydroxyl groups observed on the 600°C calcined samples is in agreement with the study of Kerr who found 0.51 moles of chemical water per Al_2O_3 in the ultrastable zeolite prepared by deep bed calcination at 500°C. Similar thermogravimetric analyses results obtained on samples (a), (b), and (f) (Fig. 1) in this laboratory are shown in Fig. 2. Again a gradual loss of weight, but no abrupt loss near 600–700°C, is observed for the stabilized sample.

In all cases, except (b), the intensity of the 3740 cm^{-1} band has increased compared to the standard hydrogen Y zeolite. The 3740 cm^{-1} band is usually attributed to silanol groups either on the external surfaces of the zeolite or due to the presence of amorphous silica containing impurities. Careful examination of the X-ray diffraction patterns suggests the increasing formation of amorphous material with increasing calcination temperature. It is also possible that silanol-type hydroxyl groups are formed by mechanism (1) above. Whatever their origin, it appears that at higher calcination temperatures, more of these silanol groups are formed rather than eliminated by condensation to Si–O–Si groups (*1*, *2*). As the lattice constant shrinks from 24.51 to 24.36, the absorbance of the 3740 cm^{-1} band increases from 0.16 to 0.26 while the calcination temperature is increased from 500 to 815°C. The characteristic absorption band near 3540–3550 cm^{-1} of hydrogen Y zeolite due to hydroxyl groups assigned to the hexagonal prisms (*9–11*) is absent. Instead, an absorption band near 3590–3570 cm^{-1} is observed. This is the strongest band in the spectrum. The band is relatively broad and naturally decreases in intensity with increasing calcination temperature. The band normally observed near 3650–3640 cm^{-1} due to hydroxyl groups formed by attachment of hydrogen to the O_1 oxygen atoms is not detected, but in all cases, except (f), a band or shoulder is observed near 3660–3670 cm^{-1}. For sample (f), a band is detected near 3610 cm^{-1}. The band is probably present in the spectra of the other stabilized samples but is not resolved. These changes in hydroxyl group spectra are not observed during the formation of stabilized magnesium hydrogen Y zeolite thus indicating different mechanisms of stabilization.

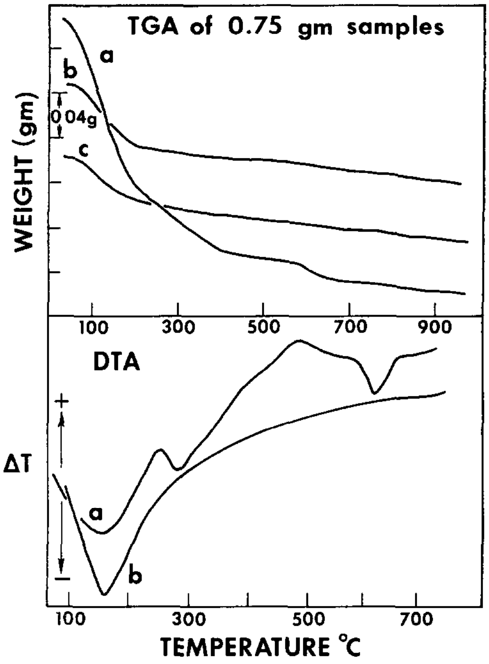


FIG. 2. Thermograms in flowing helium of (a) ammonium Y; (b) ultrastable Y [sample (b)]; and (c) ultrastable Y [sample (f)].

The results show that the structural hydroxyl groups on ultrastable Y zeolites are radically different from those of hydrogen or magnesium hydrogen Y zeolite. The characteristic hydroxyl groups attached to O_1 and O_3 oxygen atoms have been eliminated or their environments radically changed. At the same time, the population of silanol groups is markedly increased particularly with the higher calcination temperatures. When pyridine was reacted with sample (c) a sharp band was observed near 3680 cm^{-1} and the structureless absorption between 3670 and 3600 cm^{-1} was eliminated. Pyridinium ions, indicative of proton acidity, were detected on all the samples studied, thus indicating the presence of some acidic hydroxyl groups.

The locations of the newly formed hydroxyl groups are not clear at this time. The poorer resolution obtained in the spectra suggests that the hydroxyl groups are less specifically localized than in hydrogen Y zeolite. The band near 3660–3670 cm^{-1} could possibly represent AlOH groups due to $Al(OH)_3$, $Al(OH)_2^{+}$, or $Al(OH)^{2+}$ as suggested by Kerr (*1*). The nature and assignment of the lower frequency bands is uncertain.

The results show that stabilized zeolites prepared by several different methods contain silanol and other structural hydroxyl groups, which are different from those of hydrogen and magnesium hydrogen Y zeolites, even after calcination at temperatures as high as 815°C. Spectra of hydroxyl groups can be used to distinguish the different decomposition products of ammonium Y zeolites.

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JOHN W. WARD

Union Oil Company of California,
Union Research Center,
Brea, California

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The Effective Surface Area of the Promoted Vanadium Pentoxide Catalyst Supported on Silica Gel

Many authors have investigated the oxidation of sulfur dioxide on the promoted vanadium pentoxide catalyst, and have shown that the active component of the catalyst is the compound of vanadium pentoxide, potassium oxide, and sulfur trioxide (*1–3*). We have studied the rate of the oxidation of sulfur dioxide on the promoted vanadium pentoxide catalyst supported on silica gel with large surface area, and found that there is an optimum amount of the active component supported on the carrier. This result is interpreted by the concept of the effective surface area, and the rate determining step of the reaction is discussed.

The catalysts with various amount of the active component were prepared by impregnating the silica granules (0.5 ~ 1.0 mm) with a desired amount of aqueous solution of vanadyl sulfate and potassium bisulfate. The specific surface area of the silica gel was 249 m^2/g. The molar ratio of the catalyst ingredients, $V_2O_5:K_2O:SO_3$