Thermal Decomposition of Ammonium Y Zeolite

In a recent paper, Jacobs and Uytterhoeven (*1*) discuss an infrared study of "deep bed calcined ammonium Y zeolite." They conclude that "deep bed" calcination is an essential step in the preparation of the so-called ultrastable Y zeolites and that the product is not influenced in the first instance by the sodium level or aluminum deficiency. They also consider that, as also suggested by Kerr (*2*, *3*), most of the catalytic work has been reported on "deep bed" calcined samples rather than on samples of similar nature to those used in physical measurements. Kerr (*2*) initially introduced the terms shallow-bed (SB) and deep-bed (DB) calcination. He defined these terms as follow: DB, calcination in a bed of 2.3 cm diameter and 2.9 cm deep; SB, calcination in a bed of 7.0 cm diameter and 0.3 cm deep. In both cases samples were placed directly into a furnace at 500°C and heated for 1 to 4 hr. No other details are given. Jacobs and Uytterhoeven (*1*) indicate that they followed the procedure of Kerr (*2*). In the initial paper and patent of McDaniel and Maher (*4*) no calcination conditions were given, while in a later paper (*5*) heating in a static atmosphere in a muffle furnace is prescribed. It is now apparent from the patent literature that treatment of a zeolite in a steam atmosphere results in products similar to the ultrastable zeolite and in a dry atmosphere results in products similar to hydrogen Y (*6*).

In order to verify whether "deep bed" calcination is essential, samples of ammonium Y zeolite were calcined in various containers and various atmospheres. Jacobs and Uytterhoeven (*1*) seem to have omitted the significance of the atmosphere around the zeolite during the calcination, whereas Kerr (*2*) has indicated that gaseous calcination products must be removed from the zeolite environment in order that the normal hydrogen Y can be obtained. This latter point may be very significant since zeolite samples activated in catalytic reactors are usually activated in a flowing gas purge. Furthermore, neither author indicates the moisture content of their samples. As suggested by Kerr (*2*), the moisture evolved on calcination, if not free to leave the system, could result in zeolite modifications.

In our studies, three bed geometries were used: (a) a rectangular box 8 × 5 in. which had a perforated metal base. Purge gas could be passed up through the scintered base and hence through the zeolite bed. In this manner the decomposition products could be removed from the zeolite environment. For "shallow bed" calcination, the zeolite was placed in this box at a uniform 0.3 cm depth. For "deep bed" calcination, the bed depth was 3.0 cm; (b) a quartz tube of internal diameter 0.75 in. A 3-in. column of zeolite was supported on a bed of quartz wool; (c) a simple porcelain crucible of diameter 2.5 in. at the top and 1.25 in. at the base; a 1.25 in. bed of zeolite was used mixed with various amounts of water for individual experiments, and the crucible covered, and (d) a stainless steel reactor tube of 0.375 in. internal diameter. The 0.5 in. zeolite column was support on a quartz wool bed.

The zeolites were calcined dry and in steam. For a dry calcination, the sieve dried air was passed through the zeolite overnight at 120°C, the bed of zeolite was raked, and the heating continued for 4 hr. The temperature was then raised to 550°C and maintained for 4 hr. Steam calcinations were carried out by commencing to pass steam through the bed of zeolite at 120°C for 30 min, raising the temperature to 550°C and maintaining the temperature heated by placing the covered crucible in a for 4 hr. The samples in crucibles were heated by placing the covered crucible in a preheated furnace at 550°C. The samples heated in the quartz tube and reactor tube were treated similarly to those in the stainless steel box.

The ammonium zeolite had a sodium content of 1.7%, a surface area of 881 $m^2\ g^{-1}$ and a crystallinity of 90%. The zeolite contained 25% water. After calcination the zeolites were ion exchanged with a 30% solution of ammonium nitrate three times, filtered, washed and dried. The zeolites contained less than 0.15 wt % sodium. Samples of the zeolites were then recalcined "dry" and "wet" in containers 1 × 1 in. using a 1 cm bed depth. Samples of some zeolites were also recalcined "dry" without an intermediate ion exchange.

The following samples were prepared:

1. heated at 550°C in flowing steam using a 3.0 cm bed depth.
2. heated at 550°C in flowing steam using a 0.3 cm bed depth.
3. heated at 550°C in flowing dry air using a 3.0 cm bed depth.
4. heated at 550°C in flowing dry air using a 0.3 cm bed depth.
5. heated at 550°C in flowing dry air using a 3 in. bed depth.
6. heated at 550°C in static bed; zeolite contains 25% by weight of water.
7. heated at 550°C in static bed; zeolite contains 50% by weight of water.
8. heated at 550°C in static bed; zeolite contains 75% by weight of water.
9. heated at 550°C in static bed; zeolite contains 5% by weight of water.
10. heated at 550°C in flowing steam using a 3 in. bed depth.
11. heated in reactor by catalyst activation program up to 500°C.

The 550°C temperature was chosen so that comparisons could be made with the results of Jacobs and Uytterhoeven (*1*). These observations allow one to study the influence of bed depth and atmosphere more carefully. Crystallinity, surface area, unit cell dimensions, differential thermal and thermal gravimetric analyses were made. The quantitative results are listed in Table 1. Samples were made corresponding to the "SB" and "DB" products of Kerr (*2*). They had the same properties as Kerr's samples.

First, grossly comparing the samples calcined in dry air and in steam, it is seen that the steam calcined samples are much more crystalline and have a considerably greater surface area. It is also seen that the steamed samples have a unit cell constant about 0.1 Å less than the dry calcined samples. Jacobs and Uytterhoeven (*1*), Kerr (*2*), McDaniel and Maher (*4*) and Maher, Hunter and Scherzer (*5*) reported similar effects. These results are in agreement with those reported by Kerr and Shipman (*8*).

Examination of the differential thermal and thermogravimetric analyses data show similarly that the steamed sample is stabilized whereas the dry calcined sample is the normal hydrogen Y. The dry air calcined samples showed a sharp weight loss near 650°C. Kerr's "SB" sample showed a weight loss at about 670–680°C. It is also seen that the steamed samples are much more stable, after further exchange, to both calcination in steam and dry air. The steamed samples are 70% crystalline whereas the dry calcined samples are essentially amorphous. These data again indicate that the steamed samples are similar to the ultrastable Y whereas the dry calcined sample collapsed in a manner analogous to hydrogen Y. Furthermore, the unit cell constant of the steamed form, after exchange and recalcination is similar to that reported by McDaniel and Maher (*4*) and Maher, Hunter and Scherzer (*5*) for the ultrastable zeolite. No cell measurements could be made on the treated dry calcined form due to the very low crystallinity. However, the surface area of the treated dry calcined material decreased to less than 300 $m^2\ g^{-1}$ compared to over 680 for the steamed material. Hence it can be concluded that the presence of steam compared to dry air can have a dramatic effect.

The data in Table 1 show that the depth of the bed has little influence. For the steamed samples, bed depths from 0.3 cm to 2 in. made no significant differences in the physical properties. Furthermore, the

TABLE 1
PHYSICAL PROPERTIES OF TREATED AMMONIUM Y ZEOLITE

Sample treatment	(1) Calcined at 550°C			(2) (1) Hydrated in ambient air; calcined at 400°C			(3) (1) Ion exchanged			(4) (3) Calcined at 400°C in dry air			(5) (3) Calcined at 400°C in steam		
	Surf. area (m^2 g^{-1})	Cryst. (%)	Unit cell constant (Å)	Surf. area (m^2 g^{-1})	Cryst. (%)	Unit cell constant (Å)	Surf. area (m^2 g^{-1})	Cryst. (%)	Unit cell constant (Å)	Surf. area (m^2 g^{-1})	Cryst. (%)	Unit cell constant (Å)	Surf. area (m^2 g^{-1})	Cryst. (%)	Unit cell constant (Å)
Steamed at 550°C															
3.0 cm bed	743	65	24.511	718	70	24.512	750	80	24.530	772	70	24.527	679	69	24.379
0.3 cm bed	730	69	25.513	—	—	—	757	76	24.531	797	77	24.509	688	72	24.380
Dry air at 550°C															
3.0 cm bed	444	47	24.648	301	<5	—	467	46	24.624	295	<5	—	290	21	—
0.3 cm bed	496	44	24.622	169	<5	—	470	43	—	197	<5	—	367	25	24.401
3 in. bed	553	51	24.613	—	—	—	390	28	24.613	215	<5	—	269	20	—
Rapid Caln. at 550°C															
25% water	781	66	24.544	—	—	—	763	78	24.524	810	79	24.510	699	77	24.365
50% water	751	68	24.517	—	—	—	771	70	24.528	801	76	24.527	670	76	24.385
75% water	793	67	24.498	—	—	—	767	77	24.538	848	79	24.594	633	77	24.381
5% water	808	74	24.558	—	—	—	883	83	24.599	822	79	24.538	788	78	24.453
Steam at 550°C															
2 in. bed	672	68	24.463	—	—	—	789	79	24.499	784	76	24.499	698	70	24.384
Reactor activation	745	37	—	—	<5	—	—	—	—	479	<5	—	—	—	—

thermal analyses (differential and gravimetric) showed the samples to have properties similar to those of the "deep bed" calcined samples reported by Kerr (*2*) and Ambs and Flank (*7*). For the "dry air" calcined material, varying the bed depth from 0.3 cm to 3.0 in. made no significant difference in the properties of the material or in its resultant stability. There is, possibly, a trend in the data indicating a slightly more stable product as the bed depth is increased. However, the most crystalline product is still substantially less crystalline than the 0.3 cm bed steamed material. The trend with bed depth could be due to partial stabilization of the zeolite by ammonia evolved in the calcination or by small amounts of thermally evolved water being trapped in the bed. Kerr (*2, 3*) has previously suggested these causes of stabilization. Hence it can be concluded that the bed depth is not the essential factor in the preparation of ultrastable Y zeolite. Rather the atmosphere present in the vicinity of the zeolite during calcination plays a major role. The rapidly heated crucible samples show the same stabilizing effect, even when a 0.3 cm thick bed was used. However, when a similar sample was thoroughly dried and heated rapidly to 550°C, it became amorphous, again showing the need for water vapor in stabilization.

The initial calcination appears to be the major factor in determining the structural stability of the zeolite since in the second calcination, the presence or absence of steam and variations in bed depth seem to have little influence. Furthermore, calcination of a thoroughly dried sample containing 0.1% sodium at 550°C resulted in an unstable product. Hence, as indicated previously (*1, 4*), sodium level does not appear to be directly related to stability.

The data support the conclusions of Kerr (*2*) that calcination under conditions such that gaseous products are removed from the environs of the zeolite is need to produce hydrogen Y zeolite. It is obvious that the thicker or denser the sample of zeolite, the more difficult this will be to achieve. However, the results reported herein show that at a series of bed geometries, the nature of the atmosphere is dominating rather than bed depth and is a critical factor. Suitable atmospheric control can eliminate the influence of bed depth.

The studies here have considered the influence of steam or occluded water during calcination. It is quite probable, as indicated elsewhere by Kerr and Shipman (*8*), that the ammonia decomposition product might be having a stabilizing effect in some instances. However, it is known that ammonia is not a necessary atmospheric constituent since hydrogen Y, produced by acid exchange of sodium Y zeolite, can be stabilized by suitable control of the calcination technique (*9*).

In comparing catalytic measurements with physical measurement, it is often difficult to obtain identical sample conditions. However, it is unrealistic to assert that catalytic work is always done on samples treated in "deep bed" conditions (*1, 3*). As indicated above, this implied calcination by rapid heating in a stagnant atmosphere of samples presumably containing a substantial amount of physically adsorbed water. Being aware for several years (*6*) of the influence of moisture and environment during calcination, it is the usual practice in this laboratory to heat catalysts slowly in controlled atmospheres after an initial predrying. Results reported in this note show that similar calcination methods, at least in dry flowing air, produce only minor amounts if any of ultrastable Y zeolite. Furthermore, observed differences in catalytic activity of ultrastable Y and other hydrogen zeolites confirm that the materials being catalytically investigated are different (*9*).

However, in order to shed more light on this problem, a sample of ammonium Y zeolite was treated in the reactor, previously used for making catalytic measurements, in a manner analogous to that used for samples which would be monitored for catalytic activity. After removal from the reactor, the surface area and crystallinity were measured. The catalyst was also recalcined, and also ion exchanged and recalcined. Thermal analyses were also made on the samples. It is seen from the data in

Table 1 that after all stages of treatment, the properties of the sample are very similar to those of ammonium Y calcined in dry air and unlike the properties of those calcined in steam. The fact that the sample became amorphous after recalcination is very strong evidence that ultrastable Y or "deep bed" calcined Y is not formed and that the material is the normal hydrogen Y. It thus appears that previously reported catalytic measurements, at least from this laboratory, have been made on samples, which if not completely hydrogen Y contain only very minor amounts of the so-called ultrastable Y zeolite.

In conclusion, the nature of the atmosphere around the zeolite during calcination is a critical parameter determining the type of product formed, as suggested by Kerr (*2*). In a static atmosphere, the ultrastable type of zeolite is favored as the bed is deepened due to water occlusion. A flowing gas purge eliminates the bed depth phenomenon such that hydrogen Y can be produced in a "deep bed" and ultrastable type Y can be produced in a shallow bed. Analysis of samples taken from catalytic reactors indicates that they are not ultrastable or "deep bed calcined" zeolites but are hydrogen Y zeolites.

REFERENCES

1. JACOBS, P., AND UYTTERHOEVEN, J. B., *J. Catal.* **22,** 193 (1971).

2. KERR, G. T., *J. Catal.* **15,** 200 (1969).

3. KERR, G. T., AND CHESTER, A. W., *Thermochimica Acta* **3,** 113 (1971).

4. McDANIEL, C. V., AND MAHER, P. K., *Soc. Chem. Ind. London, Monogr.* 168 (1968). MAHER, P. K., AND McDANIEL, C. V., *U. S. Pat.* 3,293,192, Dec. 20, 1966.

5. MAHER, P. K., HUNTER, F. D., AND SCHERZER, J., *Advanc. Chem. Ser.* **101,** 266 (1971).

6. HANSFORD, R. C., *U. S. Pat.* 3,354,077, Nov. 21, 1967. KERR, G. T., MIALE, J. N., AND MIKOVSKI, R. J., *U. S. Pat.* 3,493,519, Feb. 3, 1970.

7. AMBS, W. J., AND FLANK, W. H., *J. Catal.* **14,** 118 (1969).

8. KERR, G. T., AND SHIPMAN, G. F., *J. Phys. Chem.* **72,** 3071 (1968).

9. WARD, J. W., unpublished data.

JOHN W. WARD

Union Oil Company of California
Union Research Center
Brea, California 92621

Received April 21, 1972

Thermal Decomposition of Ammonium Y Zeolite
A reply to John W. Ward

In his letter Ward (*16*) gives very convincing arguments to prove that during the calcination of NH_4Y zeolites the thickness of the sample on itself is not the essential factor determining the nature of the end-products, but that the composition of the atmosphere in contact with the zeolite particles is essential. With respect to the conclusions of our infrared study on deep-bed calcined NH_4Y zeolites (*1*), some apparently conflicting statements must be clarified.

We have omitted in our study to emphasize the hydrolyzing effect of the gases involved during the calcination. However, in that article we fully apply the terminology used by Kerr (*2, 3*), and Kerr, Olson and Dempsey (*4*), and the term deep-bed calcination should be understood in its original context (*2–4*) "...the calcination of NH_4Y may produce two quite different limiting cases depending upon the partial pressure of water and/or ammonia." We also clearly indicated the hydrolyzing effect by referring to the reactions proposed by Kerr (*2*). Further, the major conclusion of our work (*1*) was that the origin of the stability of deep-bed calcined samples