

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 ul-

trastable or "deep bed calcined" zeolites but are hydrogen Y zeolites.

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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

could be ascribed to the presence of aluminum ions, resulting from a partial hydrolysis of the zeolite, and located at ion exchange sites inside the small cavities.

After extended predrying times at 120°C NH_4Y samples lose most of their hydration water, and the vapor pressure due to water resulting from dehydroxylation can be kept very low by a rapid elimination of the decomposition products. This is clearly shown by Ward's data (16).

However, the question remains whether or not the gross physical properties, such as X-ray crystallinity, unit cell parameter, sorption capacity, TGA and DTA curves, are sufficient to characterize the nature of a thermally treated NH_4Y zeolite (1-7) in relation to catalysis. Hydroxyl bands near 3600 and 3700 cm^{-1} being characteristic for stabilized material (1, 5, 8, 9) it seems to us that infrared spectroscopy is a better method to decide on the presence of possibly small amounts of stabilized zeolite in thermally treated NH_4Y samples. It was shown in Fig. 7 of our original article (1), that a sample of NH_4Y , thoroughly dehydrated by a vacuum treatment at 10^{-6} Torr and subsequently heated slowly (from 25 to 500°C in 4 hr) under continuous pumping, developed besides the bands at 3650 and 3550 cm^{-1} also the bands typical for stabilized material. The geometry of this sample was deep-bed (1 cm wide and 5 cm deep), but the evacuation of the decomposition products was as good as possible. By its physical properties the sample was recognized as a typical HY. Infrared spectroscopy revealed the presence of stabilized material in not neglectable amounts. Very small amounts of water vapor seem to be sufficient to produce some stabilizing effects. It was shown by us (15) that even in thin wafers used for infrared experiments the 3600 cm^{-1} component (although small) is always generated even when the outgassing was performed carefully. CaY and LaY samples are so sensitive to hydrolysis that in the vacuum heating of very thin wafers OH groups typical for stabilized material are almost always present in appreciable amounts (15).

Taking this into account we still feel that we can subscribe Kerr's statement (2) following which some catalytic studies, interpreted as being conducted on an HY catalyst, have been done on deep-bed material. In his letter Ward proves that in the geometrical conditions of a catalytic experiment samples can be prepared having the physical properties of an HY sample. Before concluding the absence of stabilized material in reactor experiments we would prefer if the authors showed well-resolved infrared spectra of the samples after pretreatment. This is not a criticism to particular work, but only a warning that it may be dangerous to compare the results of infrared measurements (conducted on very thin samples) to catalytic experiments (conducted on a packed bed of zeolite).

At the time this warning was written down by Kerr (2) and by us (1) the remark was completely justified. The different ways of pretreatment of NH_4Y zeolites mentioned in the literature were as numerous as the authors. Many times the experimental details necessary to judge the possible presence of stabilized material are missing, especially in the earlier work when the deep-bed effects were not yet recognized (11). Uncertainties about the nature of the heated NH_4Y zeolites can sometimes raise controversies like the one appearing recently in this journal when a particular pretreatment is claimed to produce dehydroxylated material (13, 14), whereas other authors present arguments that the same treatment produces zeolites predominantly in the hydrogen form (12).

In conclusion, we agree with Ward that it is possible to avoid to a large extent the hydrolyzing effect even in geometrical conditions described as "deep-bed." However, since only a small amount of active sites are needed to make an active catalyst we still advise not to overlook the presence of small amounts of stabilized material, or of a low concentration of specific defects in HY due to a small degree of hydrolysis. Possibly a low concentration of such defects is entirely or partly responsible for the "superactivity" of the faujasites. In-

frared spectroscopy, rather than the overall physical properties can be recommended to decide on the presence of these defects.

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