limited extent. In general, however, for low degrees of exchange, hydroxyl groups giving rise to the 3650 cm^{-1} band are formed from the ammonium ions on calcination in much greater numbers than are those characterized by the 3540 cm^{-1} bands. Once we reach the point where increasing degrees of exchange remove increasing numbers of sodium ions that in the dehydrated zeolite occupy the two sites that block formation of the 3540 cm^{-1} hydroxyl groups, the relevant infrared band grows rapidly.

Finally, we wish to comment on Fig. 6 of WH. The fact that *o*-xylene isomerization increases rapidly only while protons go mainly into inaccessible positions on the O3 oxygens, despite the prior existence of a large number of accessible O1,H groups, seems to us to indicate that the presence of a few sodium ions in the supercages of the zeolite holds down the catalytic activity of the material. Thus small amounts of sodium ion, and probably other alkaline and alkaline earth cations, in positions of accessibility to incoming molecules in the zeolite supercages (sites II) may act as catalytic poisons.

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Sodium Hydrogen Y-Zeolite: Reply to Dempsey and Olson

The comments of Dempsey and Olson (*1*) [DO] on our recent paper concerning sodium hydrogen Y zeolite (*2*) [WH] are of interest. Unfortunately, they present no new data with which to support their interpretations of our original data and much of their discussion is based on somewhat irrelevant quotations from the literature.

On page 368 of WH, it is clearly stated that the locations of ammonium ions (and hence sodium ions) in sodium ammonium Y zeolites have not been reported and hence the discussion of sodium hydrogen Y zeolites is difficult. It seems to us rather naive to discuss the locations of cations in sodium hydrogen Y zeolite simply in terms of those found in hydrogen faujasite (*4*). One can question whether information derived from natural faujasite is really representative of Y zeolite because of the differences in silica to alumina ratios and the probability of cation impurity in the natural faujasite. Secondly, the locations of hydrogen in hydrogen faujasite were made by a rather indirect method which lends itself to some uncertainty. It is also not without ambiguity to attempt to interpret the locations of sodium ions in the sodium hydrogen Y zeolites in terms of the cation positions in dehydrated sodium Y (*3*) or in terms of cation locations in mixed sodium calcium faujasite (*5*). The works of Sherry (*6*) and Barrer, Davies, and Rees (*7*) clearly show that 16 sodium ions are different from the remainder. Sherry (*6*) has suggested that these 16 sodium ions are located in the small cages of the structure. Barrer *et al.* (*7*) in discussing Y zeolites, stated that in hydrated near-faujasite, 16 sodium ions per unit cell are believed to occupy positions inside the hexagonal prisms. In the absence of direct published evidence for hydrated sodium Y zeolite, the locations of these sodium ions are a matter of speculation since sodium ions are found in the hexagonal prisms of sodium X structure (*8*) but not in the sodium faujasite structure (*5, 9*). There appears to be some uncertainty in the literature as to whether Breck's data are for hydrated or dehydrated sodium Y and X (*10*). It is not stated in the original article. Barrer *et al.* (*7*) and Theng *et al.* (*11*) appear to have interpreted the data in terms of hydrated materials while Breck and Flanigen indicate that the data are for dehydrated zeolites in their later discussion (*12*). The latter interpretation, as suggested by DO, is probably, then, more correct. It is obvious from pages 368 and 369 of WH that the data have been interpreted more in the light of the ion-exchange data of Sherry and Barrer than in terms of the conflicting X-ray diffraction data of the two extreme members of the series of zeolites investigated. Fortunately, for the purpose of our discussion, it is immaterial whether the inaccessible cations are located in the hexagonal prisms and/or the sodalite portions of the structure.

The statement of DO that our data present more information about the Na^+ distribution than about the OH distribution, as a function of the sodium ion content, is difficult to understand. The primary infrared data give information about the hydroxyl groups. Hence, it is necessary to deduce the positions of the hydroxyl groups in sodium hydrogen Y zeolite before any deductions can be made about the sodium ion positions.

The discussion of paragraph 3 of DO appears to be misleading. Firstly, we made no quantitative use of Fig. 2. Secondly, if sample 1 is considered and one accepts the X-ray diffraction data of Olson and Dempsey (*4*), one sees two bands of equal absorbance representing different numbers of hydroxyl groups. The lack of a direct relationship between absorbance and number of protons forming hydroxyl groups is obvious. Furthermore, to attempt to relate the data of Fig. 2 to those of Fig. 4 seems out of place. Figure 4 shows the relative number of hydroxyl groups which are sufficiently acidic to protonate pyridine under the conditions of our experiments. It is well known to us that the acid strength of the hydroxyl groups represented by the 3640 cm^{-1} band is not constant and so, only under certain ideal conditions would one see a direct correlation between Figs. 2 and 4.

The portion of DO's comment concerning our section headed "Structural Hydroxyl Groups" is unconvincing. Firstly, it is unlikely that X-ray data on sodium, calcium faujasite (*5*), and cerium, calcium, magnesium, and sodium faujasite (*13*) shed any light on the cation positions in sodium ammonium (or hydrogen) Y zeolite. Secondly, all that the ion-exchange data of Barrer *et al.* (*7*) and Sherry (*6*) show is that there are two different types of sodium ions. It is probable that, as suggested by Sherry and by Barrer *et al.* and others, 16 of the sodium ions are located in the hexagonal prisms and/or sodalite portions of the structure and that the remaining ions are floating in the large pore section. We were perhaps too specific in attributing these accessible sodium ions to locations at the S_{II} and S_{III} positions. However, it is obvious that there is a clear relationship between the growth of the 3640 cm^{-1} band and the removal of the accessible sodium ions. Although in principle, the protons formed during deamination can move to any position in the hexagonal prism-sodalite cage network, or in fact to any other portion of the structure, they do not necessarily do so. Direct ion exchange with dilute acid produces the same pair of hydroxyl absorption bands (*14, 15*). Thus, the two methods of introduction of protons result in the formation of the same type of hydroxyl groups. Ion exchange of ammonium Y zeolite with cesium ions, which are too large to enter the hexagonal prism-sodalite cage systems, followed by deamination, eliminates the 3640 cm^{-1} band but leaves the 3540 cm^{-1} band unaffected. Thus, these hydroxyl groups are formed from production of protons in the small cage system and these protons remain in the small cage system. Furthermore, in their paper on the structure of hydrogen faujasite (4) Olson and Dempsey concluded that the hydrogens responsible for the 3540 cm^{-1} hydroxyl band are attached to the O_3 oxygen atoms and are within the hexagonal prisms. If then, some of the hydrogen responsible for the 3540 cm^{-1} band in sodium hydrogen Y zeolites is not in the hexagonal prisms, DO must consider that the 3540 cm^{-1} band represents hydrogens in different locations in fully and partially exchanged sodium Y or else they have modified their previous indirect conclusions.

The conclusion reached by DO in paragraph 5 is, apart from semantics and speculation, exactly the same as we reached; namely, that as long as a certain type of sodium ion is in the structure, the hydroxyl groups responsible for the 3540 cm^{-1} band do not form. Perhaps again we were too restrictive in associating these sodium ions with the S_I positions. However, as a logical reading of our paper and data shows, we feel that these sodium ions are best considered as being the 16 which are more difficult to ion exchange, as found by Barrer and Sherry, than the 27 cations located in the S_I and S'_I sites in dehydrated sodium Y by Eulenberger *et al.* (*3*). Moreover, our interpretation of the most suitable straight line through the data of Fig. 2, plus additional data, suggests that the 3540 cm^{-1} band starts to grow significantly during the replacement of the last 21 sodium ions. This is in reasonable agreement with the 16 ions found difficult to exchange by Sherry and Barrer and the 18 ± 2 ions found in the S'_I sites of cerium sodium faujasite by Olson *et al.* (*13*).

Concerning the comment on Fig. 6, the inhibition of the catalytic action by sodium in accessible positions had occurred to us. Such a possibility cannot be ruled out on present data. The ion-exchange data would suggest that this is not so, but in the absence of data concerning the distribution of sodium in sodium hydrogen zeolites, actually measured at reaction temperatures, we do not think a definitive conclusion is possible. However, it should also be borne in mind that measurements on several of the samples of various exchange levels discussed in WH have shown the presence of mobile protons, particularly those responsible for the 3640 cm^{-1} band (*16*). It should also be pointed out that alkaline earth and rare earth cations have been shown to promote, rather than poison, hydrogen Y zeolites (*17*).

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