the kinetic plots in Fig. 2, corresponds to 60% of the chlorosilane molecules reacting with two OH groups and 40% reacting with one OH group (exclusive of the 30% initial fast reaction). If the initial fast reaction takes place on a 1:1 basis, the overall stoichiometry is: (0.7) (1.6) + (0.3) (1.0) = 1.42, or 42% of the OH groups react 2:1 with the chlorosilane, in reasonable agreement with Evans and White's value of 31–39% which they calculated from the relative uptakes of physically and chemically adsorbed silanes. A 1.5-order kinetic function results in an almost linear plot and gives an overall stoichiometry of 35% of the OH groups reacting 2:1, which is in perfect agreement with their calculated values.

The calculations show that a kinetic evaluation of the reaction curves gives the same results as obtained by Evans and White when comparing the uptake of physically and chemically adsorbed silane. The only significant difference noted between the two studies, then, is in the values of the experimental activation energies. In our work these energies were calculated from the values of the rate constants obtained from the kinetic plots, *after the initial fast reaction has taken place,* whereas Evans and White used the half-time of reaction to determine the activation energy. Use of these half-times, however, results only in an overall value which represents the temperature dependence of the sum of the two reactions, and includes contributions from the activation energies of both the initial fast reaction and the slower coupling reaction. Unfortunately, there is insufficient published data available to recalculate the true activation energies.

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A Comment on Ward and Hansford's Paper "Active Sites on Zeolites IX"

The paper by Ward and Hansford (*1*) (WH) on the infrared bands in NaHY zeolites published recently in this journal contains some very interesting data. We feel, however, that there is an alternative and perhaps more substantial interpretation of this data than the one presented by the authors. In view of the fact that WH refers to the X-ray data of Eulenberger, Shoemaker, and Keil (*2*) (ESK) on sodium Y zeolite, and to our recent assignment of proton positions in HY (*3*), it is surprising that the authors of WH do not consider this explanation.

Despite the experimental work of ESK* giving the Na$^+$ distribution in NaY, the authors of WH rely heavily on the rather idealized site occupancies given by Breck

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[*] The data of ESK brings out the important point (see also Dempsey (*5*)) that perhaps the elusive site III cations (referred to by Breck (*4*) are more correctly site I′ cations; i.e., the energetics of the situation for monovalent cations in Y faujasites may be such that site I′ is always occupied in preference to the hypothetical site III on the square faces of the sodalite cage—even at the expense of occupying a site I and a site I′ simultaneously.

(*4*) for dehydrated (not hydrated as stated in WH) faujasite. But even though the results of ESK probably provide the better basis for a model of NaHY, we would emphasize that the Na^+ distribution in NaHY is still an open question. Given our recent assignment of OH group location in H faujasite, the WH data provide more information about Na^+ ion distribution than about OH location, as a function of sodium ion content.

From a comparison of the absorbances shown, it appears that Fig. 2 of WH can only be interpreted qualitatively; one cannot relate absorbance directly to the number of protons available for forming OH groups. This view is supported by the apparent conflict between Figs. 2 and 4 of WH. It seems probable that Fig. 4 may give a better indication of the relative increase in the number of OH groups giving rise to the 3640 cm^{-1} band between 0 and 4% sodium than does Fig. 2.

The section of the Discussion of WH headed "Structural Hydroxyl Groups" appears to us to be somewhat illogical. The preamble leading to the eighth sentence of the section in question in no way "indicates that the 3640 cm^{-1} band represents the most accessible hydroxyl groups." The study of WH may assume that the relevant OH groups are formed by replacement of the most readily exchanged sodium ions, but it is unlikely that these are located in SII and SIII positions: ion-exchange data (*6*) suggest and X-ray data (*7, 8*) show that in related systems these positions are unoccupied in the hydrated Y zeolite. Without additional information nothing can be inferred about the interaction of these hydroxyl groups with absorbing molecules. Since the protons, being point charges, cannot simply replace the sodium ions in sites I, but must move to different positions, they can, in principle, move to any positions within the hexagonal prism/sodalite cage network. Thus it cannot be inferred, because the 3540 cm^{-1} band is presumed to be associated with removal of sodium ions from site I in the hexagonal prisms, that the hydrogens, produced by dehydration and deamination of the partially exchanged zeolite, also lie within the hexagonal prisms.

The situation seems to us to be as follows. After partial exchange of ammonium ion into a sodium Y zeolite, there will exist a certain, undetermined distribution of sodium and ammonium cations in various degrees of hydration, some localized in the structure, some not. During calcination, water and ammonia molecules are lost, and the remaining sodium cations and protons redistribute themselves. The results of WH indicate that while sodium ions remain in the structure they preferentially occupy sites where they prevent local formation of those hydroxyl groups that give rise to the 3540 cm^{-1} band. Our assignment of this band (*3*) associates protons with O3 oxygens in such a way that the protons lie near the planes at which the hexagonal prisms meet the sodalite cages. Since cations in either the site I *or the sites I′* of a given hexagonal prism coordinate to O3 oxygens, they will block the association of protons with the relevant O3 oxygens, and no contribution to the infrared band at 3540 cm^{-1} will arise from this hexagonal prism. ESK (*2*) show that there are per unit cell in sodium Y zeolite, 8 cations in sites I, and 19 in sites I′—a total of about 27 cations that presumably must be removed before the 3540 cm^{-1} band can reach its maximum intensity. Drawing the best straight lines through the 3540 cm^{-1} data of Fig. 2 of WH, it may easily be verified that the 3540 cm^{-1} band increases rapidly in intensity while the last 25 or so Na cations are being replaced by protons. This strongly suggests that at the 4% sodium level most of the sodium ions in NaHY occupy sites I and I′. In other words, it appears that the replacement by protons of sodium ions that in the calcined state would occupy sites II does not essentially alter the distribution of sodium ions found by ESK in the small pore system (hexagonal prisms and sodalite cages) of the zeolite. If sodium ions do not completely block formation of the 3540 cm^{-1} hydroxyl groups, these groups will form to whatever extent they can, since it has been shown (*9, 10*) that, of the two groups, these hydroxyls have the lower acidity. Figure 2 of WH shows that this occurs to a 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