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A Reexamination of the Hypothesis of Breck and Skeels Concerning the Reinsertion of Aluminum in the Framework of Dealuminated Y Zeolites

In a series of papers Breck *et al.* (*1–4*) have dealt with the thermal decomposition products of NH_4Y zeolites. Some of their conclusions refer to the stabilization process of the zeolite Y structure. The authors deduce that non-framework aluminum species are reinserted into the vacant sites of the dealuminated framework by treatment with either NaOH solution or by prolonged treatment in salt solution. The stabilization effect of the procedure A of McDaniel and Maher (*5*) is explained by the reinsertion reaction.

This interpretation of the stabilization process of the Y structure seems to be doubtful. Samples prepared by original and modified procedures of McDaniel and Maher have been investigated by us and other authors using high-resolution ^{29}Si and ^{27}Al NMR (*6–9*) and ir (*10*) spectroscopy. A progressive removal of aluminum from the framework of the starting material and intermediate products was detected and an increase of the content of framework aluminum has never been found in these investigations. The thermal stability of the dealuminated Y zeolites increases continuously with increasing framework Si/Al ratio up to 1180°C for a faujasite structure almost free of aluminum (*11*). Therefore, the aluminum content (framework or non-framework) seems not to play an important role in the stabilization of the Y zeolites.

As demonstrated recently, high-resolution ^{29}Si NMR spectroscopy permits a direct insight into the structural changes after modification of NH_4Y zeolites, in that it allows the direct determination of the quantitative distribution of the various $Si(OSi)_{4-n}(OAl)_n$ building units and the Si/Al ratios of the tetrahedral zeolite framework (*9, 12*). Moreover, information on Si,Al ordering in the zeolite framework can be derived from the ^{29}Si NMR spectra (*12, 13*). Decomposition products of NH_4Y zeolites in the presence of steam, including samples obtained by the procedure of McDaniel and Maher, were studied by us extensively, but no reinsertion of aluminum could be detected (*8, 9, 12, 13*).

In order to check whether a reinsertion process of aluminum takes place under the specific conditions used by Breck and Skeels we have prepared samples under almost the same conditions and have investigated them by solid state ^{29}Si NMR and ir spectroscopy.

We started with NaY zeolite (Si/Al = 2.5) and exchanged it with ammonium ions to an extent of 85%. The $NaNH_4Y$-85 sample was transformed into DB-400 by deep-bed treatment at 400°C. The ^{29}Si NMR spectrum of DB-400 (spectrum A) reveals that the Si/Al ratio of the framework is increased to 3.6, i.e., dealumination has occurred. Then we have used exactly the same treatment as described by Breck and Skeels (*2*) which results in the "filtrate" sample (by slurrying of DB-400 in NaCl solution—spectrum B) and in the "slurry" sample (by slurrying of DB-400 in NaCl solution followed by titration with NaOH to pH 10—spectrum C).

The ^{29}Si NMR spectra of the samples A,

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B, and C shown in Fig. 1 are very similar and a constant Si/Al ratio of the tetrahedral zeolite framework of 3.6 has been estimated from the spectra of the three samples. The reinsertion of about 20% of the total aluminum content into the framework of sample C as discussed by Breck and Skeels (*3*) would cause considerable changes in the peak intensities of the spectrum. For comparison in Fig. 1 the ^{29}Si NMR spectrum of the untreated $NaNH_4Y$ sample (spectrum D) is included. A similar spectrum has to be expected if the total amount of non-framework aluminum is reinserted into the framework of sample C as claimed by Breck and Skeels. It is obvious that also a smaller extent of realumination should be reflected by the spectra. Consequently, we have to conclude that no noticeable reinsertion of nonframework aluminum into the framework of sample C occurs during the alkaline treatment.

TABLE 1

Framework Infrared Frequencies

Sample	$\tilde{\nu}$ (cm^{-1})		
Results of Breck and Skeels			
$NaNH_4Y$-86	1010	787	573
"Filtrate"	1024	795	583
"Slurry"	1019	791	579
Results of this work			
$NaNH_4Y$-85	1145	790	577
DB-400	1160	805	582
DB-400 "filtrate"	1155	800	580
DB-400 "slurry"	1150	797	580

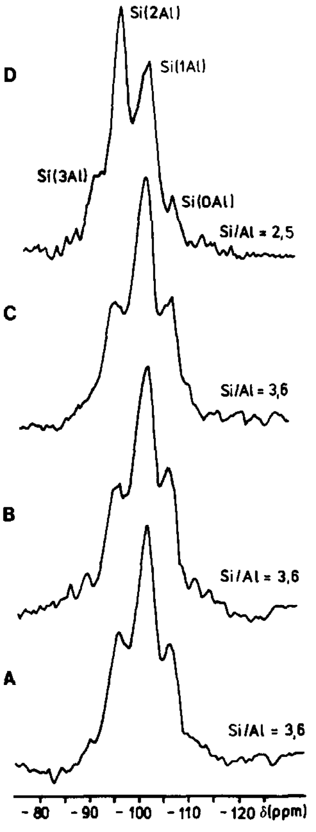

FIG. 1. ^{29}Si NMR spectra of zeolite samples. (A) DB-400. (B) DB-400 "filtrate." (C) DB-400 "slurry." (D) $NaNH_4Y$-85. (The spectra were obtained on a Bruker CXP-200 spectrometer at 39.74 MHz using single pulses (flip angle 30°) with 5-s repetition, magic angle spinning at 3 kHz and strong dipolar proton decoupling. For each spectrum 1000 scans were accumulated. Chemical shifts δ in ppm from tetramethylsilane, high-field shifts negative.)

The conclusion of Breck and Skeels concerning the reinsertion of aluminum in vacant framework sites was deduced from differences in chemical composition between "filtrate" and "slurry" sample and, furthermore, from very small differences in framework infrared frequencies and unit cell constants.

The framework infrared frequencies, measured by Breck and Skeels and in this work, are summarized in Table 1. As may be seen, the decrease of the wavenumbers from the "filtrate" to the "slurry" sample is confirmed by our measurements. However, a decrease of the wavenumbers is already observed at the transition from DB-400 to DB-400 "filtrate" caused by the NaCl treatment. For the interpretation it must be taken into account that the framework infrared frequencies depend not only on the aluminum content but also to a minor extent on the sodium content, as shown by Stock (*14*). Therefore, the decrease of the infrared frequencies can be explained by reexchange of Na^+ ions against protons. Of course, the existence of the HY zeolite is accepted in this interpretation (*15, 16*). Our investigations show that a weak dealumination cannot be avoided in the preparation of HY by deammoniation of NH_4Y, but nevertheless the main part of the structure consists of HY zeolite and its protons are exchangeable for Na^+ ions (*17*).

The small increase of the unit cell constant of Breck and Skeels' "slurry" sample is probably within the limit of error which is not specified by the authors.

The results of chemical analysis presented by Breck and Skeels give no evidence of the reinsertion of aluminum into the framework because the chemical analysis determines the total amount of aluminum and cannot differentiate between framework and non-framework aluminum. It is confirmed by our experiments that up to 10% of the total aluminum is dissolved in the acidic "filtrate" solution. The increasing aluminum content in the "slurry" sample observed by Breck and Skeels is probably caused by precipitation of $Al(OH)_3$ in the alkaline medium.

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G. Engelhardt
U. Lohse

Central Institute of Physical Chemistry
Academy of Sciences of the GDR
DDR-1199 Berlin-Adlershof
Germany (DDR)

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