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Cation Assisted Lattice Improvement of Highly Siliceous ZSM-5 upon Prolonged Heat Treatment

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Prolonged heat treatment of highly siliceous, template-free ZSM-5 containing Na^+ or K^+ causes improvement of the lattice structure, migration of alkaline ions to the outer layers of the zeolite particles as shown by XPS and an increased isolation of ≡ Si-ONa sites from ≡ Si-OH sites, as shown by ^{29}Si CP MAS NMR analyses of silylated products.

Recently, much effort has been concentrated on the changes taking place in the lattices of ZSM-5 zeolites upon heating. Most studies agree that during heat treatment at or above 530 °C dealumination, 1) phase transitions (orthorhombic to monoclinic and vice versa)2) and ring closure by condensation of silanol sites 3) determine the spectral appearances e.g. in ^{29}Si MAS NMR of the products. The role of cations was usually not discussed. Here, we propose an ordering of the lattice assisted by alkaline ions which, in turn, move selectively towards the outer layers of the zeolite particles.
The ZSM-5 zeolites were prepared according to standard procedures4,5) but without addition of aluminium compounds. Removal of TPA^+ by calcination (3 h at 550 °C), subsequent washing with H_2O and drying yields the starting material. Chemical analyses gave Si/Al > 4000 and Si/Na between 60 and 125, depending upon the synthesis procedure. Heat treatments were carried out in normal laboratory air at 550 °C. XRD patterns indicated high crystallinities and monoclinic framework symmetries of all samples. Figures 1A and 2A show that the spectral resolutions in ^{29}Si MAS NMR and IR of the starting material are relatively poor. Moreover, the ^{29}Si MAS NMR signal at about -102 ppm on Fig. 1A indicates the presence of Q^3 sites (silicon atoms coordinated with only three siloxy groups) in this material. After prolonged heating (68 h at 550 °C) highly resolved spectra were obtained and Q^3 sites are not longer detectable. Figure 1B represents one of the best resolved ^{29}Si MAS NMR spectra of ZSM-5 observed at Bo = 7 T. The spectral resolution in ^{29}Si MAS NMR or IR of ZSM-5 strongly depends on the number and

positions of structural elements present in the material. Randomly distributed aluminium atoms and lattice defects give extra contributions to the number of structural elements and consequently lead to a broadening of the spectra.[6,7) As our zeolites already exhibit a low aluminium content and ^{27}Al MAS NMR investigations (not shown) did not indicate any loss of framework Al during prolonged heating we attribute the improvement of spectral resolution to a loss of lattice defects. Heat treatment of the starting material after repeated ion exchange with solutions of NH_4NO_3 or HCl (Si/Na > 1200) resulted in poorly resolved ^{29}Si MAS NMR and IR spectra, comparable with those on Figs. 1A and 2A. Material back-exchanged with solutions of NaOH or KOH before heat treatment gave highly resolved spectra. Moreover, heat treatment in accurately dried air

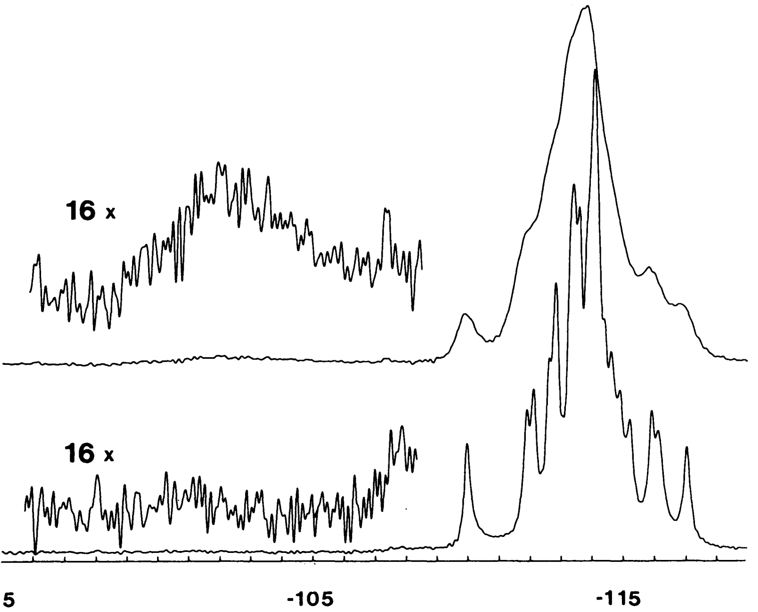


Fig.1. ^{29}Si MAS NMR spectra of starting material before (A) and after (B) 68 h at 550 °C (on a Bruker CXP-300 spectrometer at 59.63 MHz, ca 4kHz MAS rotation).

(instead of normal laboratory air) shows that besides alkaline ions the presence of water molecules is required to obtain highly ordered ZSM-5 materials.

In order to clarify the fate of the ≡ Si-OH sites during the heat treatment we carried out a series of silylations with subsequent product analyses by ^{29}Si CP MAS NMR. These silylations with trimethylchlorosilane at 400 °C decreased the internal volumes of all samples to about 80% (measured by n-butane sorption), indicating that silylation (also) occured inside the zeolite pores. In a primary reaction step trimethylchlorosilane $ClSi(CH_3)_3$ can react with ≡ Si-OH or ≡ Si-ONa groups with formation of trimethylsiloxysilane $(\equiv SiO)Si(CH_3)_3$ and HCl or NaCl. Secondary and tertiary products can be formed by a subsequent reaction between the methyl groups of trimethylsiloxysilane and silanol groups in the zeolite lattice (with concomitant evolution of methane) if the latter are present at suitable distances. In general, the silylation products can be described by the

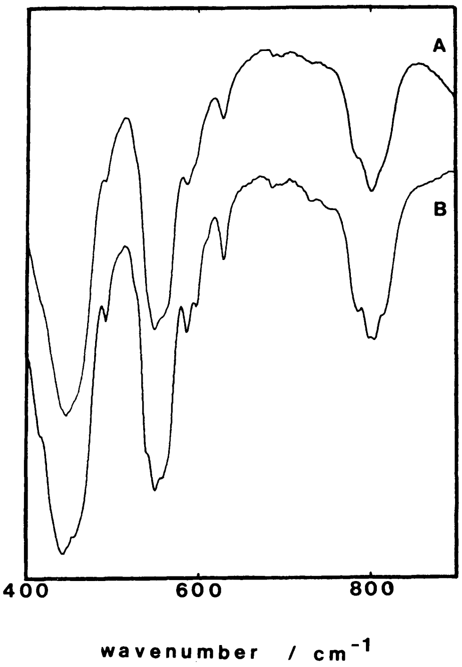


Fig.2. FT IR spectra of starting material before (A) and after (B) 68 h at 550 °C on a Bruker IFS 113 v spectrometer with wafers from 1 mg zeolite in 200 mg KBr).

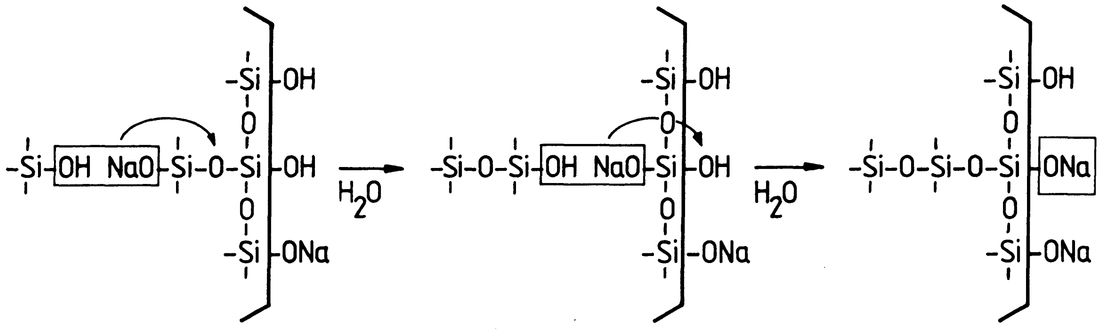
formula $(\equiv SiO)_nSi(CH_3)_{4-n}$ with n from 1 to 3. The ($\equiv$SiO) units or siloxy groups have their origin in $\equiv$Si-ONa and/or $\equiv$Si-OH groups of the zeolite lattice whereas the rest stems from trimethylchlorosilane. The different products can be distinguished by means of ^{29}Si CP MAS NMR. Primary products (n = 1) resonate at + 12 ppm, secondary products (n = 2) at about - 18 ppm and tertiary products (n = 3) at about - 66 ppm [8]. Our silylated starting material shows ^{29}Si NMR signals at - 18 ppm and - 66 ppm belonging to secondary and tertiary silylation products. The primary trimethylsiloxysilanes (+ 12 ppm) were only obtained by silylation of samples heated 68 h at 550 °C. In addition, secondary and tertiary products were found, the total amount of silylation products is now clearly smaller. We conclude that ZSM-5 zeolites without prolonged heat treatment contain $\equiv$ Si-ONa or $\equiv$ Si-OH moieties with at least one or two $\equiv$ Si-OH groups at distances suitable for formation of bi- and tridentate linkages. In conjunction with the rather low overall concentration of terminal groups this implies a form of clustering. XPS shows that during heat treatment of the starting material Na^+ ions move selectively towards the outer surface of the zeolite particles except, of course, the amount required for charge balance of the AlO_2^- groups in the lattice (Table 1). The following scheme may illustrate our results and conclusions (next page):

Table 1.

XPS Results

Sample	$\frac{\text{Intensity Na (1s)}}{\text{Intensity Si (2p)}}$[a]
Starting material	0,097
68 h 550 °C	0,132

a) The intensity of Na (1s) peaks (binding energy 1074 eV) are related to the intensities of Si (2p) peaks (binding energy 106 eV) as an internal standard, assuming that the concentration of Si atoms does not change during heat treatment.



(1) **(2)** **(3)**

Without prolonged heat treatment ZSM-5 zeolites contain considerable amounts of clustered terminal groups in the lattice and, of course, at the outer surface of the particles (1). After prolonged heating the zeolite lattice is found to be highly ordered, the number of clustered terminal groups has decreased and sodium ions concentrate at the outer surface of the particles (3). As this favourable effect of heat treatment can only be achieved in the presence of alkaline ions and water molecules we conclude that mobile alkaline ions can attack neighbouring siloxane bridges whereas the covalently bonded hydrogen in silanols is rather immobile. By attack and hydration of siloxane bridges and subsequent condensation of the so-formed or initially existing silanols to "new" siloxane bridges bond rearragements are achieved (2). After sufficiently long heating a highly ordered ZSM-5 lattice with a minimum number of structural elements and defects is obtained. Accurate description of the structural elements would require interpretation of the spectral information which is, in our view, not feasible at present. We wish to thank S.M.A.M. Bouwens for the XPS measurements. We are indebted to G. Rutten for his advice regarding the silylation experiments. This investigation was supported by the Netherlands Organisation for the Advancement of Pure Research (ZWO).

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