

²⁹Si-MAS NMR Studies of Hydrothermal Dealumination of Zeolite ZSM-20

Michael Stöcker,^{a,*} Stefan Ernst,^b Hellmut G. Karge^c and Jens Weitkamp^d

^aDepartment of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, B.C., V6T 1Y6, Canada, ^bDepartment of Chemistry, University of Oldenburg, Ammerländer Heerstrasse 114–118, D-2900 Oldenburg, ^cFritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6, D-1000 Berlin 33 and ^dInstitute of Chemical Technology I, University of Stuttgart, Pfaffenwaldring 55, D-7000 Stuttgart 80, F.R.G.

Stöcker, M., Ernst, S., Karge, H. G. and Weitkamp, J., 1990. ²⁹Si-MAS NMR Studies of Hydrothermal Dealumination of Zeolite ZSM-20. – Acta Chem. Scand. 44: 519–521.

Increasing efforts have been devoted to the synthesis and characterization of zeolite ZSM-20 during the last few years.^{1–4} Recently, models for the structure have been proposed.^{5,6} According to these models, zeolite ZSM-20 is a random intergrowth of the cubic faujasite structure and its hexagonal variant, also called Breck's Structure Six (three letters code BSS).

ZSM-20 was first described by Ciric^{7,8} and later by Vallyocsik.⁹ Since then, this zeolite has been of great interest, especially for catalysis. Compared to faujasite (X- and Y-zeolite), ZSM-20 can be synthesized with a higher Si/Al ratio, leading to a better thermal and hydrothermal stability, an increased acid strength and an improved deactivation profile during some catalytic reactions. Therefore, much work is presently directed towards making highly siliceous ZSM-20 either by direct synthesis or dealumination of Al-rich materials. Solid-state ²⁹Si-MAS NMR spectroscopy should be an excellent tool for monitoring such a dealumination. So far, only in one paper has the ²⁹Si-MAS NMR spectrum of a synthesized ZSM-20 (with a Si/Al-ratio of 4) been presented.¹ This paper reports a detailed study of the dealumination of ZSM-20, using solid-state ²⁹Si-MAS NMR spectroscopy.

Experimental

Zeolite ZSM-20 was crystallized in the manner described in Ref. 4. The X-ray powder pattern of the as-synthesized material is presented in Fig. 1. HZSM-20 was obtained by air calcination at 530°C for 16 h, twofold ion-exchange with a 0.5 M aqueous solution of NH₄Cl for 2 h at 100°C, and a second air calcination for 16 h at 530°C. This parent

material for the dealumination studies was further characterized by IR spectroscopy using a Perkin-Elmer 225 spectrometer (Fig. 2).

Dealumination of HZSM-20 was achieved by steaming the sample with air saturated with water vapour at atmospheric pressure using the following temperature/time conditions: 550°C for 16 h and afterwards 700°C for 5 days. The ²⁹Si-MAS NMR spectra were recorded on a Bruker MSL-400 FT NMR spectrometer, operating at 79.5 MHz and using a single 90° pulse sequence. The following conditions were applied: sweep width 20 kHz, pulse width 5 μs (90°), 8K data points, number of scans ~ 320, repetition time 5 s, 7 mm rotor, spinning frequency ~ 3 kHz.

Results and discussion

The results of the IR spectroscopic characterization of HZSM-20 are shown in Fig. 2. After activation of the sample for 12 h at 350°C in high vacuum, two bands appear in the region of the OH stretching frequencies, viz. at ca. 3550 and 3640 cm⁻¹, respectively. The positions and relative intensities of the two bands are comparable to those which are usually obtained with Y-type zeolites. Upon pyridine adsorption at 200°C, the band at 3640 cm⁻¹ disappears. From the known structure of ZSM-20 and by analogy with Y-type zeolites this band can therefore be assigned to OH groups vibrating into the large supercage. The band at 3550 cm⁻¹ can be attributed to OH groups inside the sodalite cages which are not accessible for pyridine molecules.

Upon adsorption of pyridine, its typical deformation bands appear between 1300 and 1800 cm⁻¹. From the high intensity of the band at 1542 cm⁻¹ in comparison with the intensity of the band at 1455 cm⁻¹ it can be concluded that Brønsted acid sites clearly predominate in the HZSM-20 sample over Lewis acid sites.

* To whom correspondence should be addressed. Present address: Center for Industrial Research, P.O. Box 124, Blindern, N-0314 Oslo 3, Norway.

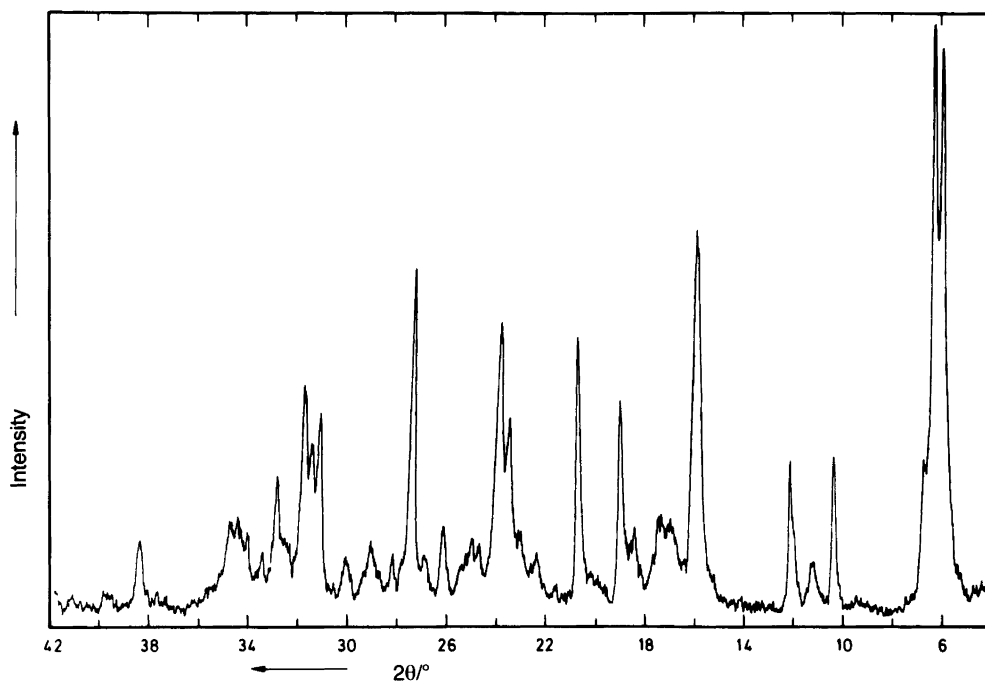


Fig. 1. X-Ray powder pattern of as-synthesized ZSM-20 ($\text{CuK}\alpha$ radiation).

The ^{29}Si -MAS NMR spectra taken after the various treatments of zeolite ZSM-20 are shown in Fig. 3. The spectrum of the as-synthesized and calcined material consists of three distinct lines corresponding to Si atoms with two [Si(2Al) at ~ -96 ppm], one [Si(1Al) at ~ -102 ppm] and zero aluminium atoms [Si(OAl) at ~ -108 ppm] in their next coordination sphere. With ZSM-20, the signals were observed at somewhat higher fields compared to the corresponding lines for faujasite type zeolites, indicating that ZSM-20 is a more siliceous material than NMR Y-zeolite. For the as-synthesized ZSM-20 sample, the evaluation of the NMR spectrum gave a lattice Si/Al ratio of 3.9, in line with earlier results reported by Derouane *et al.*¹ Furthermore, the ^1H - ^{29}Si -CP/MAS spectra were recorded of ZSM-20, but did not yield additional information of

interest, since the template has been removed during calcination.

As shown in Fig. 3, ion exchange with NH_4Cl led to a small dealumination (spectrum b versus spectrum a), recognizable by an increased intensity of the high-field signal [Si(OAl)]. Calcination at 530°C (spectrum c) brings about a considerable dealumination, as indicated by the fact that the low-field line [Si(2Al)] has almost disappeared. The dealumination proceeds deeply as steaming is continued at elevated temperatures (spectra d and e). Finally, a single sharp resonance line is obtained, representing the Si(OAl) site. From an NMR point of view, this result indicates the existence of only one crystallographic inequivalent T-site for the lattice elements Si and Al. Our results correspond well with the recently published structure of ZSM-20.^{5,6}

The disappearance of Al is accompanied by sharpening of the resonance lines (lower half-widths in spectra d and e, compared with a-c), since the dipolar interactions between silicon and aluminium (Al has a quadrupole moment) are increasingly lacking. It can, furthermore, be seen from the broad line (with low intensities in spectra d and e) that dealumination of ZSM-20 by steaming causes the formation of some amorphous material.

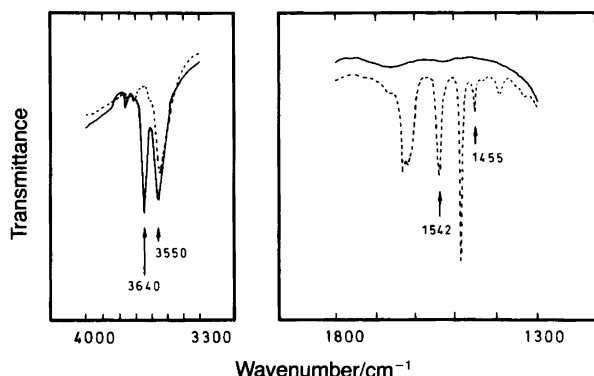


Fig. 2. IR spectroscopic characterization of the parent HZSM-20 material after activation for 12 h at 350°C in high vacuum (full lines) and after subsequent adsorption of pyridine at 200°C (dotted lines).

Acknowledgements. M.S. is indebted to Prof. C. A. Fyfe (University of British Columbia, Vancouver, Canada) for his kind cooperation during the author's stay in Vancouver. The Norwegian Council for Scientific and Industrial Research (NTNF) is gratefully acknowledged for financial support (fellowship). J.W. and S.E. express their thanks for financial support by the *Deutsche Forschungsgemeinschaft*, *Fonds der Chemischen Industrie* and *Max Buchner-Forschungstiftung*.

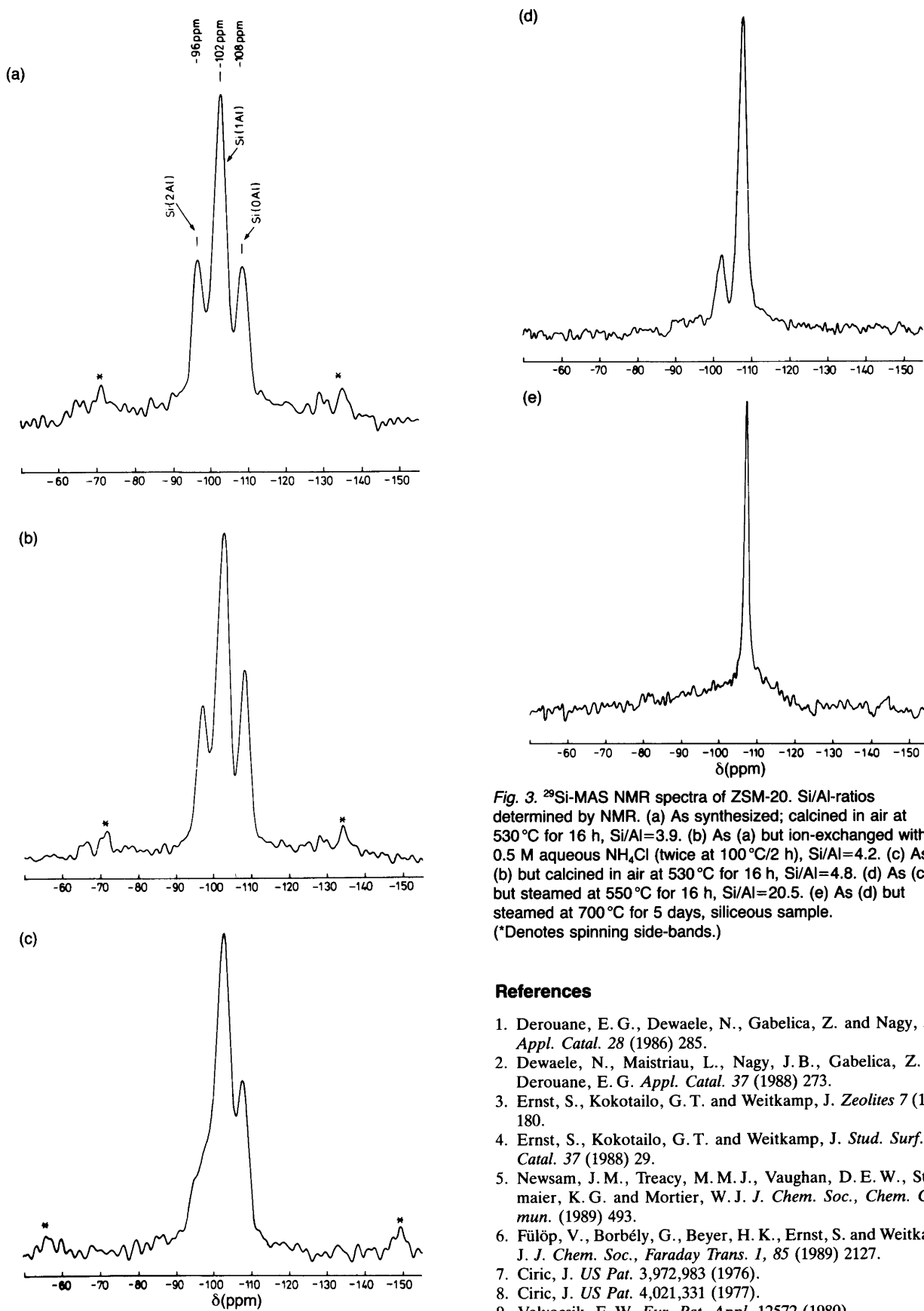


Fig. 3. ^{29}Si -MAS NMR spectra of ZSM-20. Si/Al-ratios determined by NMR. (a) As synthesized; calcined in air at 530°C for 16 h, Si/Al=3.9. (b) As (a) but ion-exchanged with 0.5 M aqueous NH_4Cl (twice at $100^\circ\text{C}/2$ h), Si/Al=4.2. (c) As (b) but calcined in air at 530°C for 16 h, Si/Al=4.8. (d) As (c) but steamed at 550°C for 16 h, Si/Al=20.5. (e) As (d) but steamed at 700°C for 5 days, siliceous sample. (*Denotes spinning side-bands.)

References

1. Derouane, E. G., Dewaele, N., Gabelica, Z. and Nagy, J. B. *Appl. Catal.* 28 (1986) 285.
2. Dewaele, N., Maistriau, L., Nagy, J. B., Gabelica, Z. and Derouane, E. G. *Appl. Catal.* 37 (1988) 273.
3. Ernst, S., Kokotailo, G. T. and Weitkamp, J. *Zeolites* 7 (1987) 180.
4. Ernst, S., Kokotailo, G. T. and Weitkamp, J. *Stud. Surf. Sci. Catal.* 37 (1988) 29.
5. Newsam, J. M., Treacy, M. M. J., Vaughan, D. E. W., Strohmaier, K. G. and Mortier, W. J. *J. Chem. Soc., Chem. Commun.* (1989) 493.
6. Fülöp, V., Borbély, G., Beyer, H. K., Ernst, S. and Weitkamp, J. *J. Chem. Soc., Faraday Trans. I*, 85 (1989) 2127.
7. Ciric, J. *US Pat.* 3,972,983 (1976).
8. Ciric, J. *US Pat.* 4,021,331 (1977).
9. Valyocsik, E. W. *Eur. Pat. Appl.* 12572 (1980).

Received December 8, 1989.