

Short Communication

^{29}Si and ^{27}Al MAS NMR Study of a Zeolite Single Crystal

Michael Stöcker

SINTEF SI, PO Box 124 Blindern, N-0314 Oslo, Norway

Stöcker, M., 1993. ^{29}Si and ^{27}Al MAS NMR Study of a Zeolite Single Crystal. – Acta Chem. Scand. 47: 935–936.

Single crystals of zeolites in the range of a few millimetres in size (or larger) have not yet been synthesized. A number of attempts to prepare large single crystals of zeolites have been tried, either under higher or lower gravity or with other changes in the synthesis procedure.^{1–3} As yet, all efforts to prepare large single crystals of zeolites have been unsuccessful. However, natural zeolites often occur as single crystals, and we report here for the first time a solid-state ^{29}Si and ^{27}Al MAS NMR investigation of a chabazite single crystal. The origin of this crystal is traced back to Oberstein an der Nahe (Germany); the size of the investigated single crystal was measured as about 3 mm (Fig. 1), and its weight was determined as 32 mg.

The solid-state MAS NMR spectra were recorded on a Varian VXR 300 MHz spectrometer, equipped with a Jakobsen MAS probe using a 7 mm zirconia rotor. The Si/Al ratio of the crystal was checked by microprobe to be 2.4. The crystal structure of chabazite is well described, and data on the rhombohedral cell ($R\bar{3}m$), including X-ray data, have been published elsewhere.⁴

The ^{29}Si MAS NMR spectrum of a single crystal of chabazite (Fig. 2) consists of five signals representing the

different numbers of aluminium atoms in the second coordination sphere of the single crystallographic non-equivalent Si site. The chemical shifts have been measured as -110.0 ppm [Si (0Al)], -104.2 ppm [Si (1Al)], -98.6 ppm [Si (2Al)], -93.6 ppm [Si (3Al)] and -88.8 ppm [Si (4Al)]. The small hump on the low-field side of the Si (4Al) signal is due to noise. The recorded chemical shift values are in the range expected for zeolites as powders. The relative intensities of the Si (n Al) lines can be used to calculate the framework Si/Al ratio in zeolites. The framework Si/Al ratio of the investigated chabazite single crystal was determined by NMR to be 2.2, which is somewhat lower than the overall value of 2.4. Obviously, a small amount of Si exists in non-framework positions (amorphous?), which is not unusual for minerals. The linewidths of the two largest signals at

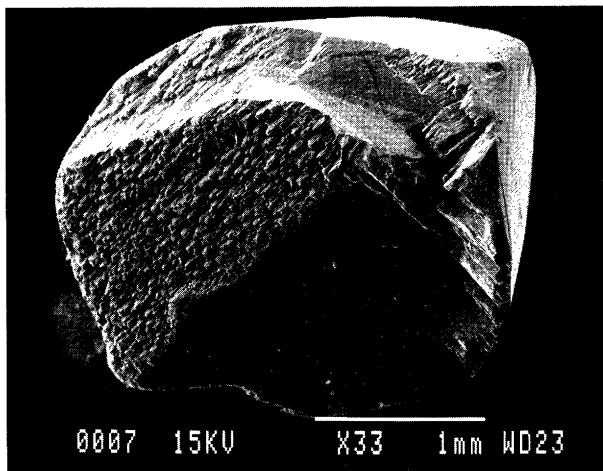


Fig. 1. SEM micrograph of a single crystal of chabazite zeolite.

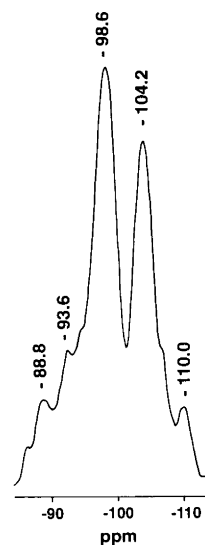


Fig. 2. ^{29}Si MAS NMR spectrum of a single crystal of chabazite zeolite. Recording conditions: frequency, 59.591 MHz; sweep width, 14 kHz; pulse width, 7.5 μs (90° pulse); repetition time, 5 s; acquisition time, 1 s; number of scans, 13 528; MAS spinning speed, 5.0 kHz. The lines were referenced to the low-field signal of ZSM-5 equal to -109.6 ppm.

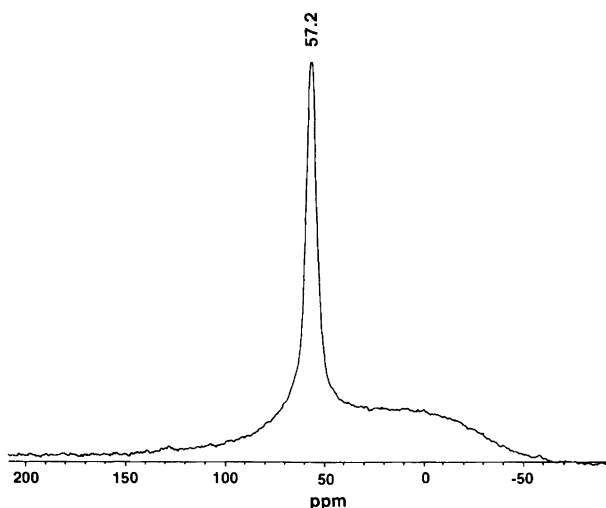


Fig. 3. ^{27}Al MAS NMR spectrum of a single crystal of chabazite zeolite. Recording conditions: frequency, 78.157 MHz; sweep width, 50 kHz; pulse width, 2.0 μs (90° pulse: 6.5 μs); repetition time, 1 s; acquisition time, 0.05 s; number of scans, 1000; MAS spinning speed, 5.5 kHz. The lines were referenced to the signal of 1 M aluminium nitrate solution equal to 0 ppm.

−104.2 and −98.6 ppm have been measured as 137 and 167 Hz, respectively. The ^{27}Al MAS NMR spectrum (Fig. 3) reveals a sharp signal at 57.2 ppm, representing tetrahedrally (framework) coordinated aluminium. The broad signal with a low intensity is due to the Al

background of the zirconia rotor. The linewidth of the Al signal was determined as 463 Hz.

The results of this single-crystal NMR investigation of a zeolite are in line with those obtained for zeolite powders in general. However, this study demonstrates the utility of solid-state MAS NMR for single-crystal studies of zeolites. The critical point is the placement of the single crystal in the rotor without disturbing the balance during the magic-angle spinning at 5.5 kHz.

Acknowledgments. We are indebted to the Royal Norwegian Council for Scientific and Industrial Research and the Norwegian Space Center for financial support of this work.

References

1. Hayhurst, D. T., Melling, P. J., Kim, W. J. and Bibbey, W. *ACS Symp. Ser.* 398 (1989) 233.
2. Stöcker, M., Akporiaye, D., Andersen, A. G., Lillerud, K. P., Seip, K. L. and Rønneid, T., *Adv. Space Res.* 11 (1991) 357.
3. Guth, J. L., Kessler, H. and Wey, R. In: Murakami, Y., Iijima, A. and Ward, J. W., Eds., *New Developments in Zeolite Science and Technology*, Kodansha, Tokyo, and Elsevier, Amsterdam, 1986, p. 121.
4. Von Ballmoos, R. and Higgins, J. B., *Zeolites* 10 (1990) 368S. Meier, W. M. and Olson, D. H. *Atlas of Zeolite Structure Types*, Butterworth-Heinemann, London 1992, p. 72.

Received November 27, 1992.