MFI High-Al ZSM-5 Si(93), Al(7)

Contributed by Hans Lechert and Ralph Kleinwort

Verified by A. Palmqvist, J. Brendle and H. Kessler

Type Material $Na_7[Al_7Si_{89}O_{192}] : wH_2O$

Method H. Lechert, R. Kleinwort [a]

Batch Composition 3.25 Na_2O : Al_2O_3 : 30 SiO_2 : 958 H_2O (exclusive of seeding gel)

Source Materials

distilled water
sodium hydroxide (Merck, pure)
tetrapropylammonium hydroxide (Fluka, 20% solution)
silicic acid (Merck, technical grade, SiO_2 : 0.5 H_2O)
sodium aluminate (Roth, Al_2O_3 : 1.24 Na_2O : 0.57 H_2O)

Seeding Gel Preparation[b]

(1) [710.3 g water + 13.8 g sodium hydroxide + 117.0 g TPA-OH solution], dissolve and mix thoroughly
(2) [(1) + 158.9 g silicic acid], add silica in portions under stirring. Shake the resulting mixture for one hour at ambient temperature. Age at 100˚C for 16 hours

Synthesis Gel Preparation (for ~-87 g product)

(1) [867.8 g water + 8.8 g sodium hydroxide + 10.3 g sodium aluminate], dissolve and mix thoroughly
(2) [(1) + 113.1 g silicic acid], add silica in portions under stirring. Shake vigorously for one hour at ambient temperature
(3) [(2) + 50 g seeding gel],[c] shake for one hour

Crystallization

Vessel: 50 mL PTFE-lined stainless steel autoclaves
Temperature: 180˚C [d]
Time: 40 hours [e]
Agitation: none

Product Recovery

(1) Recover product by filtration
(2) Wash thoroughly with distilled water
(3) Dry at 105˚C for 24 hours
(4) Pulverize dried product in an agate mortar [f]

Product Characterization

XRD: fully crystalline MFI[g,h] competing phase: mordenite (at lower Si/Al ratios in the gel)
Elemental Analysis: Si/Al = 12 to 13.5[i]
Crystal Size and Habit: 6 μm crystals

References

[1] G. Bellussi, G. Perego, A. Carati, U. Gomaro, V. Fatore, in Innovation in Material Science, P. J. Grobet, W. J. Mortier (eds.), Elsevier, Amsterdam, 1988

[2] H. Kacirek, A. Meyer, German Patent 3 402 842 Al

[3] R. Kleinwort, PhD Thesis, University of Hamburg (1995)

[4] A. Nastro, C. Coflella, R Aiello, in Stud. Surf. Sci. Catal. Vol. 24, B. Drzaj, S. Hocevar, S. Pejovnik (eds.), Elsevier, Amsterdam, 1985, p 19

[5] J. M. Berak, R Mostowcz, in Stud. Surf. Sci. Catal., VoL 24, B. Drzaj, S. Hocevar, S. Pejovnik (eds.), Elsevier, Amsterdam, 1985

[6] W. Schwieger, K. H. Bergk, U. Haedcke, German Patent 2 83 1 26 (1990)

[7] H. P. Rieck, German Patent OS 3 242 352 (1984)

[8] P. Chu, F. J. Rosinski, European Patent Appl. 110650 (1983)

Notes

a. According to Bellussi, [1] the ZSM-5 structure crystallizes in batches of the composition: $NaAlO_2$ n[$Na_mH_{4-m}SiO_4$] pH_2O in the ranges n = 20 to 50, m = 0.1 to 0.2 and p = 400 to 500. For m < 0.1, generally amorphous products were observed. Above m = 0.2, mordenite crystallizes. For n <20, ferrierite was found and above n = 50, zeolite Q. The Si/Al ratio in the product was nearly equal to the Si/Al in the batch. Compared to batches with template, those without template usually show a distinctly enhanced crystallization time. The enhancement is especially due to an increased induction period, leading to the conclusion that the crystallization should be carried out with the use of seeds. Another hope of the application of seeds is that the area of the formation of ZSM-5 in the crystallization field can be extended to higher m and lower n by suppressing the formation of mordenite which crystallizes preferably in that region.

b. A quite active seeding agent is obtained by carefully aging a gel giving silicalite. [2] For this gel, only a small amount of TPA-OH is necessary which does not influence the Si/Al ratio of the final product.

c. Good results have been obtained using 1-10 wt% seeding gel in the mixture.

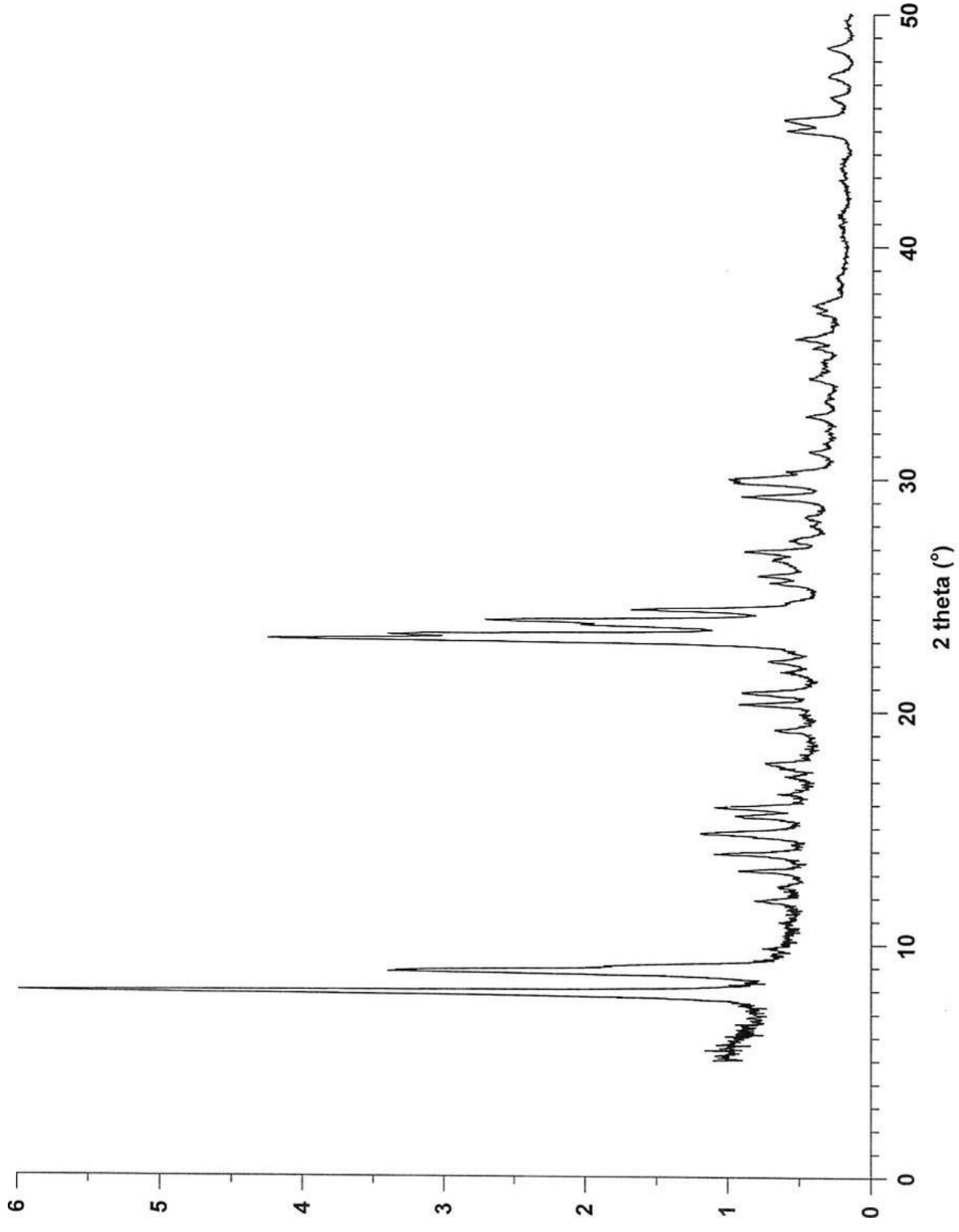
d. Good results have been obtained at temperatures from 145°C to 190°C. At 190°C, the crystallization is finished at about 10 hours.

e. The crystallization kinetics have been checked by comparison of the crystallinity with an industrial sample by X-ray. [3]

f. The final products were kept in a desiccator over saturated $CaCl_2$ solution for 24 hours before further characterization.

g. The kinetic experiments showed that the described seeding gel led to a drastically reduced induction period of crystallization and to a considerable increase in the crystallinity of MFI. This shows that the area of MFI crystallization can be extended into the range where mordenite or ferrierite has been found.

h. Crystallinity of the products was determined by comparing the sum of the peak areas between $2\theta = 23.2^\circ$ and 24.5° with that of a well-crystallized industrial sample which was used as a standard throughout the experiments.

i. For lower Si/Al ratios in the batch, mordenite could not be avoided. For higher Si/Al ratios in the batch, Si/Al of the products increased but remained slightly below Si/Al of the batch. Further information about the crystallization of MFI in template-free systems can be found in references [4-8].

MFI **High-alumina ZSM-5** **Si(93), Al(7)**