A ^{29}Si N.M.R. Study of the Ultrastabilization Process in Synthetic Faujasite

Ian E. Maxwell,* Wilbert A. van Erp, Gary R. Hays, Ton Couperus, Rob Huis, and A. Derek H. Clague

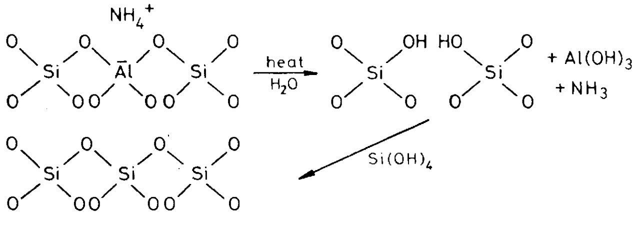
Koninklijke/Shell-Laboratorium, Amsterdam, P.O. Box 3003, 1003 AA Amsterdam, (Shell Research B.V.), The Netherlands

The removal of aluminium from the zeolite framework of the ammonium form of synthetic faujasite during calcination has been observed using solid-state ^{29}Si n.m.r. spectroscopy.

Ultrastabilization, a heat treatment whereby the thermal stability of the hydrogen form of synthetic faujasite (HY) can be markedly increased, was first reported by McDaniel and Maher.[1] This procedure involves a hydrothermal treatment of the ammonium-exchanged form of synthetic faujasite, NH_4Y, under carefully controlled conditions. The resultant ultrastable HY zeolite is of particular interest as a solid acid catalyst which exhibits a high level of activity for a variety of cracking reactions.

Since the discovery of ultrastabilization, there have been numerous studies aimed at an understanding of the mechanism of this process. In addition to the increase in thermal stability during the stabilization procedure, the following major observations[2,3] have been made: (i) stabilization is more readily achieved in the presence of steam; (ii) there is an associated decrease in the crystal unit cell dimensions; (iii) the process is facilitated in samples with low levels of residual sodium; (iv) the stabilized zeolite has a decreased ion exchange capacity; (v) aluminium can be readily acid-leached from the stabilized zeolite without loss in crystallinity.

Perhaps the most widely accepted explanation of ultrastabilization which is consistent with the above observations involves the removal of aluminium from the zeolite framework during the hydrothermal treatment and its replacement by silicon[3] (Scheme 1). However, this mechanism is by no means fully confirmed and a number of important questions remain unanswered, such as the origin of the silica which is required for the second step.



Scheme 1

Recently, there has been interest in the application of ^{29}Si solid-state magic angle n.m.r. spectroscopy for studying the ordering of aluminium in various zeolites.[4-6] In the present study we have made use of this technique to observe directly the modification of the zeolite framework during the ultra-

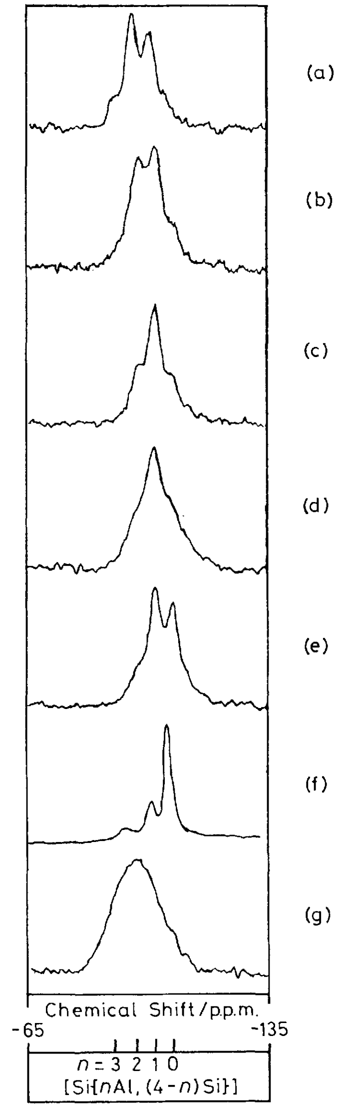


Figure 1. ^{29}Si Solid-state n.m.r. spectra after various treatment stages. (a) NH_4Y; (b) after calcination at 400 °C for 1 h; (c) after calcination at 500 °C for 1 h; (d) After calcination at 400 °C for 1 h in the presence of steam; (e) After calcination at 500 °C for 1 h in the presence of steam; (f) After calcination at 750 °C for 1 h in the presence of steam; (g) NaY after calcination at 750 °C for 1 h in the presence of steam. The spectra were obtained on Bruker CXP-300 and CXP-200 spectrometers using single pulses (waiting time between acquisitions 30 s) and employing magic angle spinning (rates between 3 and 4.5 kHz). The number of acquisitions varied between 1000 and 2000 for 100 mg of sample. Chemical shifts are given using powdered quartz as reference (−107.4 p.p.m. to an external sample of liquid tetramethylsilane).

stabilization treatment. The starting material was a commercial sample (Union Carbide, Y62) of ammonium-exchanged synthetic faujasite with a SiO_2/Al_2O_3 ratio of 4.8 and a residual Na_2O content of 2.5 %w.

The ^{29}Si n.m.r. spectrum of the parent ammonium-exchanged form, NH_4Y, is shown in Figure 1(a). Four peaks are readily discernible, which, on the basis of previous studies,[4–6] can be attributed to framework silicon in a tetrahedral co-ordination surrounded by silicon or aluminium in various ratios, *i.e.* for this series: [Si(3Al, Si)], −90.5 p.p.m.; [Si(2Al, 2Si)], −95.6 p.p.m.; [Si(Al, 3Si)], −101.5 p.p.m.; [Si(4Si)], −106.9 p.p.m.

Calcination of the NH_4Y zeolite has been carried out at various temperatures in both the presence and the absence of steam. The ^{29}Si n.m.r. spectra of the resultant HY zeolites are shown in Figures 1(b)—(f), from which it is evident that substantial changes have occurred with respect to the distribution of aluminium in the zeolite framework. In fact, even under relatively mild conditions (heating for 1 h at 400 and 500 °C) and in the absence of steam there is a significant decrease in the [Si(2Al, 2Si)] peak and a corresponding increase in the [Si(Al, 3Si)] component [Figures 1(b) and (c)]. In the presence of steam this process is considerably accelerated, such that the [Si(4Si)] peak becomes much more pronounced [Figures 1(d)—(f)].

Thus, these results provide evidence of the removal of aluminium from the zeolite framework in both the presence and the absence of steam. It therefore seems likely that even during the relatively dry calcination conditions used for simple deammination to form the unstabilized HY zeolite, some loss of aluminium from the framework will occur.

X-Ray measurements indicate that all the samples described thus far remain crystalline upon treatment. The broad resonances in Figure 1(d), for example, are therefore almost certainly due to a distribution of chemical shifts rather than loss of crystallinity and the presence of amorphous material. A blank experiment carried out by heating a sample of NaY (Union Carbide Y-52, SiO_2/Al_2O_3 = 4.7, 13 %w Na_2O) at 750 °C, in the presence of steam resulted in a totally amorphous material [Figure 1(g)].

The data, however, do not discount a stabilization mechanism under hydrothermal conditions whereby aluminium vacancies are replaced by silicon which is derived from a recrystallization process rather than *via* migration of occluded or surface silica, as has been previously suggested.[2,3] The recrystallization mechanism remains plausible in view of the large amount of extra-framework silica required to fill the aluminium vacancies, the distribution of chemical shifts, and hence the range of slightly different structures present when ultrastabilization has not been fully completed, together with the high degree of crystallinity of the resultant, steam-treated, ultrastabilized samples. This high crystallinity is evidenced by the relatively narrow ^{29}Si n.m.r. peaks [see for example, Figure 1(f)].

In conclusion, these results demonstrate the potential of ^{29}Si solid-state n.m.r. as a technique for studying not only structural aspects of zeolites but also their chemistry.

Added in proof: Since this work was submitted it has come to our notice that Engelhart *et al.*[7] have also applied ^{29}Si solid-state n.m.r. techniques to the process of dealumination.

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