

## Powder Neutron Diffraction and $^{29}\text{Si}$ MAS NMR Studies of Siliceous Zeolite-Y

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IN HONOR OF SIR JOHN MEURIG THOMAS ON HIS 60TH BIRTHDAY

Powder neutron diffraction results are presented for two forms of zeolite Y: a sample of Na-Y with a Si/Al ratio of 2.61 ( $Fd\bar{3}m$ ,  $a = 24.703(1) \text{ \AA}$ ) and a sample of siliceous-Y ( $Fd\bar{3}m$ ,  $a = 24.2576(3) \text{ \AA}$ ) which was prepared from dealuminated Y by washing with water and acid followed by subsequent heat treatment. Both zeolites are highly crystalline and show no other crystalline impurities. The structural effects that are caused by the removal of sodium ions and framework aluminium are clearly indicated by changes in the  $T\text{-O}$  bond distances and temperature factors and related changes in the  $\text{O-T-O}$  and  $T\text{-O-T}$  angles. We examine the influence of hydration on the  $^{29}\text{Si}$  spectrum of the purely siliceous material and describe our attempts to determine the location of adsorbed benzene in this material. © 1993 Academic Press, Inc.

### Introduction

Dealuminated zeolites have received considerable attention due to their enhanced thermal stability and catalytic properties. Of particular industrial importance is dealuminated, or ultrastable, Y, which is the mainstay of the petroleum cracking industry (1). Various methods of dealumination, including treatment with steam, acids, volatile halides, and chelating agents, have been devised (2). The use of silicon tetrachloride vapor has the advantage that this mild dealumination process leaves a material that retains nearly all of the original crystallinity (3).

Dealuminated Y (DAY) has been studied

by several techniques, most successfully by NMR spectroscopy. This has helped in the identification of detrital material that is present after the dealumination (4), as well as in the characterization of the structural defects that the treatment causes (5). Another important method of characterizing zeolites is by neutron powder diffraction studies combined with Rietveld refinement techniques (6). One such study of dealuminated Y on a sample that still had a relatively large amount of aluminum present (the Si/Al ratio was approximately 11) has been reported (7).

In this paper we report the results of a high-resolution time-of-flight neutron powder diffraction experiment on a siliceous faujasite. The Na-Y starting material was treated with silicon tetrachloride vapor and subsequently washed and heated to create a "zero defect" faujasite structure (ZDDAY). The sample has previously been studied by

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$^{29}\text{Si}$  NMR and IR spectroscopies (5). The resulting material presents a number of interesting opportunities both for computer modeling and for experiments in which the influence of exchangeable cations on adsorption and other properties can be explored. For comparative purposes, we present structural data on a sample of Na-Y with a Si/Al ratio of 2.61. Although similar results have been reported elsewhere (8), in this work we give details of a significantly more precise refinement. Both samples were examined in the dehydrated state. We also discuss the results of a low-temperature neutron study on a sample of ZDDAY containing adsorbed benzene.

## Experimental

### Sample Preparation

Dealuminated Y was synthesized as described previously (5), and the ZDDAY was prepared by heating the DAY to 550°C for 8 hr in air. The  $^{29}\text{Si}$  NMR of this material showed only a  $-108.0$  ppm peak,  $\text{Si}(\text{OSi})_4$ , and was free of NMR-detectable defects (see below). The sample of Na-Y was kindly supplied by Laporte Industries, and a Si/Al ratio of 2.61 was determined from X-ray fluorescence spectroscopy and confirmed by  $^{29}\text{Si}$  NMR.

### Neutron Diffraction Studies

Both samples were dehydrated for approximately 12 hr at 300°C under a dynamic vacuum prior to being loaded into the vanadium-walled cans. The transfers were performed in a glove bag filled with dry nitrogen. A third sample was prepared by adding deuterobenzene to the dehydrated ZDDAY, at a loading of approximately one molecule per supercage.

Data for the ZDDAY samples were collected at the 1-m position on the high-resolution powder diffractometer at the Rutherford-Appleton Laboratory's pulsed neutron source, ISIS. In the case of the

ZDDAY/benzene sample, the data were collected at 4 K. Rietveld refinements were performed using the CCSL software codes (9), employing a Voigtian peak shape and a five-term Chebyshev polynomial for the background. The model of Broussard and Shoemaker (10) was used as the starting point for refinements in space group  $Fd\bar{3}m$  with the origin at the center of symmetry. Neutron scattering lengths were taken from Ref. (11). For all of the atoms, the appropriate fractional coordinates and isotropic temperature factors were successfully refined; in addition, the silicon site occupancy was included in the final model.

The data for Na-Y were collected on the  $D1a$  diffractometer at the Institute Laue-Langevin, Grenoble. The refinement was performed with the POWDER (12) suite of programs and selected subroutines from the Cambridge Crystallographic Subroutine Library (13). The peak shape was modeled as a two-term asymmetric Voigt, based on the works of Howard (14) and van Laar and Yelon (15), and the background was estimated visually. The scattering factor for the  $T$  site was based on a Si/Al ratio of 2.61. In this refinement, overall isotropic temperature factors were used for the  $T$  site, oxygens, and sodiums. Estimated standard deviations in the bond distances and angles were computed from the errors in the atomic coordinates using the program ORFFE (16).

### Magic Angle Spinning NMR Measurements

Silicon spectra were acquired on a Varian VXR-400 spectrometer operating at 9.4 T. A Chemagnetics MAS probe was used to spin 7.5-mm (o.d.) samples at a speed of 7 kHz. A 45° pulse (4.5  $\mu\text{s}$ ) and a 30-sec delay were used to acquire 120 to 1800 transients into 1K data points. After a line broadening of 20 Hz was applied, the spectra were zero-filled to 8K, giving a final resolution of about 5 Hz per data point. Chemical shifts are referenced to

TABLE I  
DETAILS OF THE REFINEMENTS

Sample	Na-Y (Si/Al = 2.61)	ZDDAY
Temperature (K)	298	298
Diffraction method	Constant wavelength	Time-of-flight
Wavelength Å	2.98	—
<i>d</i> range	1.58–17.8	0.8–2.8
Space group	<i>Fd3m</i> , origin at center	<i>Fd3m</i> , origin at center
<i>a</i> (Å)	24.703(1)	24.2576(3)
Zeropoint	−0.298(2) <sup>o</sup>	7.0(7) μs
<i>R</i> <sub>E</sub>	5.69	2.16
<i>R</i> <sub>P</sub>	7.86	2.63
<i>R</i> <sub>wp</sub>	8.10	3.09
<i>X</i> <sup>2</sup>	2.03	2.04
Si occ	—	0.980(6)
<b><i>R</i>-factor definitions</b>		
$R_E = 100[\{N - P + C\}/\sum w_i (y_i^o)^2]^{1/2}$		
$R_P = 100[\sum  y_i^o - y_i^c /\sum y_i^o]$		
$R_{wp} = 100[\sum w_i  y_i^o - y_i^c ^2/\sum w_i (y_i^o)^2]^{1/2}$		
$X^2 = (R_{wp}/R_E)^2$		

Note.  $y_i^o$  are the background-corrected observed point intensities,  $y_i^c$  are the calculated point intensities,  $N$  is the number of observations,  $P$  is the number of refined parameters,  $C$  is the number of constraints, and  $w_i$  are the weights ( $=1/\sigma_i^2$ ).

TMS using hexamethyldisiloxane (6.7 ppm) as an external reference.

## Results and Discussion

### Neutron Diffraction Studies on Na-Y and ZDDAY

Details of the neutron diffraction refinements for Na-Y and ZDDAY are presented in Table I, refined atomic parameters in Table II, and distances and angles in Table III. The final observed, calculated, and difference plots are shown in Figs. 1 and 2. The good *R* factors and relatively flat difference profiles confirm that the refinements are satisfactory and that no crystalline impurities are present, although the ZDDAY sample appears to contain small amounts of amorphous material, as indicated by slight humps in the background of the raw data. The results for Na-Y are in good agreement with those from previous studies (8).

It is of interest to compare the cubic lat-

tice parameters of the two structures (Table I), since it is well known that the values decrease with increasing Si/Al ratio, due to a change in the *T*-site atomic radii, and that an approximately linear relationship exists between  $a_0$  and the Al content (17). The value predicted for hydrated sodium Y with a Si/Al ratio of 2.61 is 24.65 Å, and that for a completely dealuminated Y is 24.19 Å. These are consistent with the observed values for our dehydrated samples.

The average *T*-O bond distance for Na-Y, 1.642 Å, is in excellent agreement with that calculated (1.639 Å) for a Si/Al ratio of 2.61, assuming Si-O and Al-O bond distances of 1.60 and 1.74 Å, respectively. Similarly, the average Si-O distance found in the ZDDAY agrees well with the expected value. It is interesting to note the range of *T*-O distances in the two materials. For the sample of Na-Y, the distances span a range of 0.049 Å and the shortest distance is to the oxygen atom, O(1), which does not bond to any of the sodium cations; the other three

TABLE II  
 ATOMIC PARAMETERS FOR Na-Y AND ZDDAY

Atom	Position	x	y	z	B(iso)	Site occ.
Na-Y						
Si/Al(1)	192i	-0.0547(1)	0.1246(1)	0.0356(1)	1.12(6)	
O(1)	96h	0.0000	-0.1062(1)	0.1062(1)	2.14(3)	
O(2)	96g	-0.0020(1)	-0.0020(1)	0.1423(1)	2.14(3)	
O(3)	96g	0.0737(1)	0.0737(1)	-0.0323(1)	2.14(3)	
O(4)	96g	0.0718(1)	0.0718(1)	0.3185(1)	2.14(3)	
Na(1)	16c	0.0000	0.0000	0.0000	1.6(4)	0.27(2)
Na(2)	32e	0.0545(3)	0.0545(3)	0.0545(3)	1.6(4)	0.48(1)
Na(3)	32e	0.2352(2)	0.2352(2)	0.2352(2)	1.6(4)	0.91(2)
ZDDAY						
Si(1)	192i	-0.05392(8)	0.12530(8)	0.03589(9)	0.37(6)	0.980(6)
O(1)	96h	0.0000	-0.10623(6)	0.10623(6)	1.16(6)	
O(2)	96g	-0.00323(6)	-0.00323(6)	0.14066(9)	1.42(6)	
O(3)	96g	0.07570(6)	0.07570(6)	-0.03577(9)	1.33(5)	
O(4)	96g	0.07063(7)	0.07063(7)	0.32115(10)	0.74(6)	

distances are significantly longer. This trend arises from a decrease in the  $T-O$  bonding interaction caused by additional coordination of the oxygens to the sodium ions. For the ZDDAY, the range of Si-O distances is much narrower, as expected, but subtle differences do remain.

The average  $O-T-O$  angle for the two samples is approximately  $109^\circ$ , and again the variation of angles is much greater for Na-Y than for the siliceous sample. The variations in  $T-O-T$  angles also reflect the influence of the cations, with the angle at O(1), which carries no sodium ions, being almost identical in both samples, whereas those at O(2), O(3), and O(4) show marked relaxation as a result of the removal of the cations. For ZDDAY, the site occupancy of the tetrahedral site refined to yield a final value of 0.980(6); we do not regard the deviation from unity as being significant, especially in the light of the  $^{29}\text{Si}$  NMR results (see below). The Debye-Waller factors are higher in Na-Y than in ZDDAY (Table II), an observation that we ascribe to the disordered nature of Na-Y, which will give rise to additional contributions to the apparent temperature factors as a result of static displacements.

 TABLE III  
 DISTANCES ( $\text{\AA}$ ) AND ANGLES ( $^\circ$ ) IN Na-Y AND ZDDAY, WITH ESDS

	Na-Y (2.61)	ZDDAY
$T(1)-O(1)$	1.613(3)	1.607(2)
$T(1)-O(2)$	1.658(4)	1.597(2)
$T(1)-O(3)$	1.662(4)	1.604(2)
$T(1)-O(4)$	1.633(4)	1.614(3)
Mean $T-O$	1.642	1.605
$O(2)-T(1)-O(4)$	105(1)	108.7(2)
$O(2)-T(1)-O(1)$	113(1)	110.7(1)
$O(2)-T(1)-O(3)$	105(1)	108.7(2)
$O(4)-T(1)-O(1)$	111(1)	108.2(1)
$O(4)-T(1)-O(3)$	112(1)	111.5(2)
$O(1)-T(1)-O(3)$	111(1)	109.1(1)
Mean $O-T-O$	109	109.5
$T(1)-O(1)-T(1)$	138(1)	138.4(2)
$T(1)-O(2)-T(1)$	144(1)	149.3(2)
$T(1)-O(3)-T(1)$	138(1)	145.8(2)
$T(1)-O(4)-T(1)$	148(1)	141.4(2)
Mean $T-O-T$	142	143.7
Na(1)-O(3)	$6 \times 2.696(2)$	
Na(2)-O(2)	$3 \times 2.932(8)$	
Na(2)-O(3)	$3 \times 2.252(8)$	
Na(3)-O(2)	$3 \times 2.370(6)$	
Na(3)-O(4)	$3 \times 2.864(6)$	

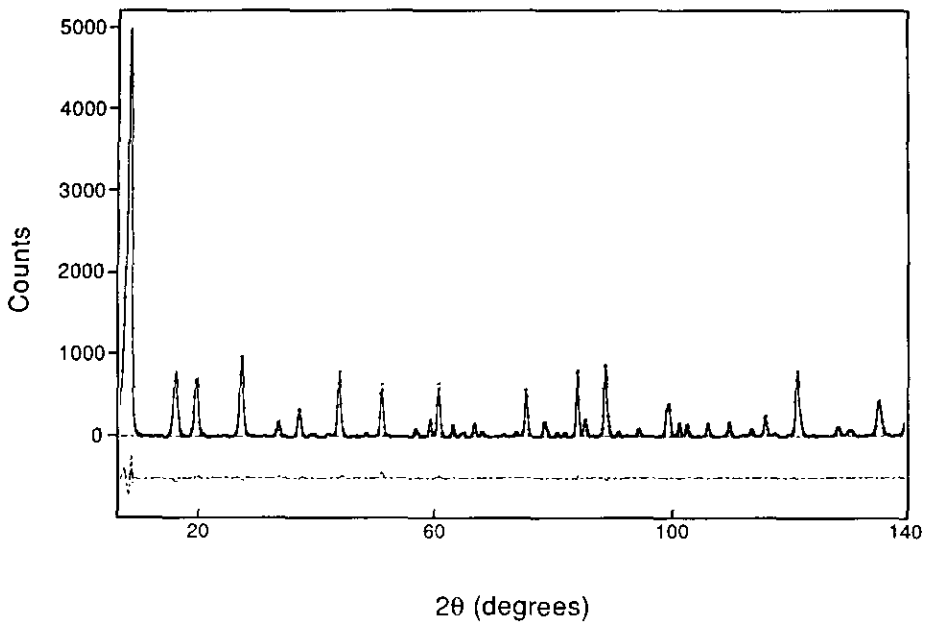


FIG. 1. Observed (dots), calculated (solid line), and difference (at bottom) profiles for sodium zeolite-Y, Si/Al = 2.61.

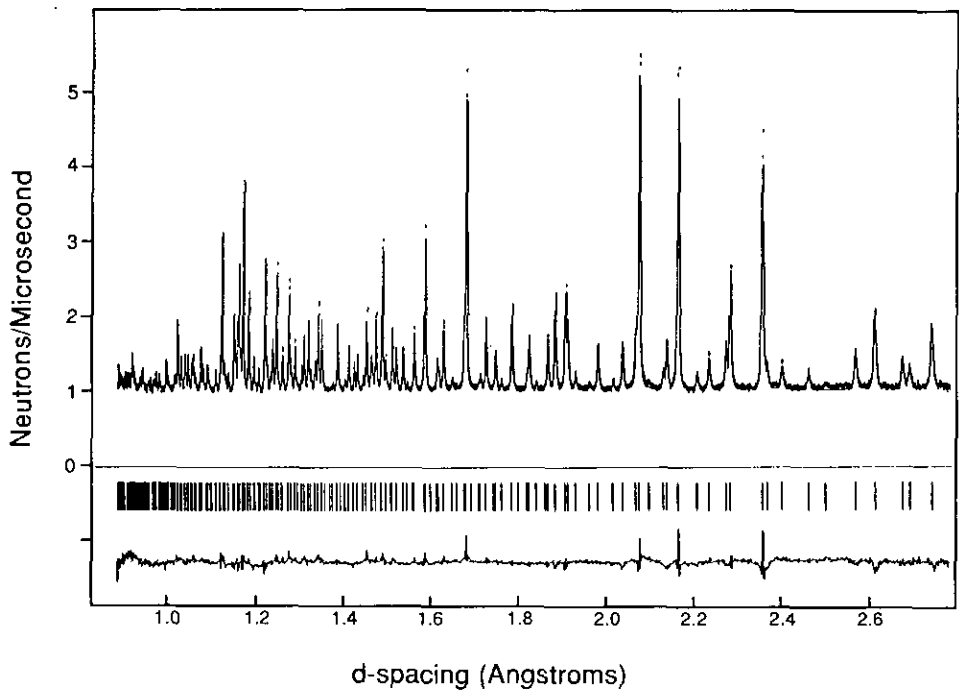


FIG. 2. Observed (dots), calculated (solid line), and difference (at bottom) profiles for siliceous zeolite-Y (ZDDAY). The reflection positions are marked above the difference profile.

### Neutron Diffraction Studies on ZDDAY/Benzene

Since it is firmly established (18) that benzene molecules are adsorbed preferentially at the SII cation site on the threefold axis in dehydrated Na-Y, the purpose of the neutron study on the ZDDAY/benzene sample was to establish the location of the sorbate in the absence of cations. Rather unexpectedly, we found that the powder neutron diffraction data for the ZDDAY/benzene sample are virtually indistinguishable from the parent ZDDAY pattern, and it is not surprising therefore that an excellent refinement ( $R_p = 2.55\%$ ) could be obtained without the inclusion of the benzene sorbate. The atomic coordinates reveal only minor changes from those of the parent structure. Initially these observations were attributed to the loss of benzene from the sample, perhaps by cryopumping during cooling, but the increase in the lattice parameter from 24.2576 Å to 24.2823 Å, in spite of the decrease in temperature, indicates that this is not the case. We now believe that our inability to detect the benzene in this system stems from the fact that the potential energy surface is flatter in the absence of sodium, and that the benzene is distributed over a range of lower symmetry sites that are displaced from the threefold axis; this would considerably reduce the influence of the sorbate on the Bragg intensities. We note that recent  $^2\text{H}$  NMR measurements of this system (19) are indicative of behavior that is intrinsically different from that observed in Na-Y, and we are currently performing Monte Carlo simulations to test our hypothesis.

### $^{29}\text{Si}$ MAS NMR Spectra

The  $^{29}\text{Si}$  MAS NMR spectrum of dehydrated ZDDAY is shown in Fig. 3a. The silicon spectrum of a dried sample (100°C for 16 hr) of ZDDAY gave only a single peak at -108.4 ppm, and no change was observed when the sample was exposed to air for several days. However, when two

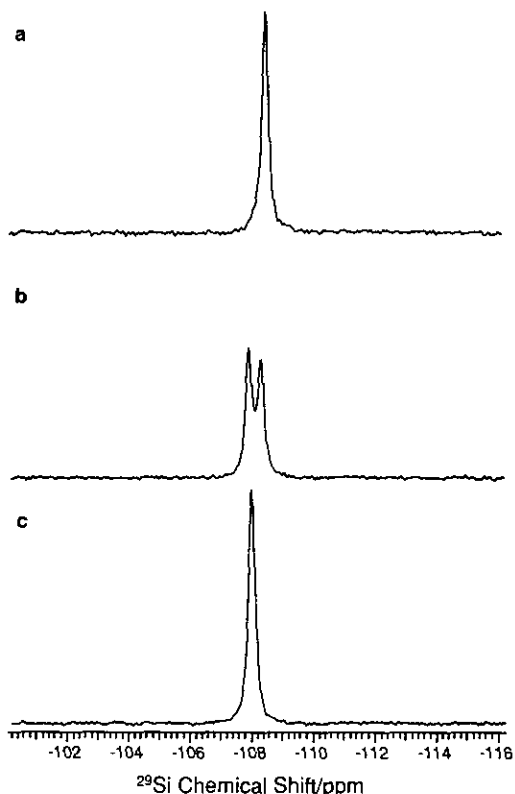


FIG. 3.  $^{29}\text{Si}$  MAS NMR spectra of ZDDAY in different states of hydration: (a) dehydrated sample; (b) and (c) samples with increasing water content (see text).

drops of water were added to the sample, an additional peak at -108.0 ppm was detected, and in an immediate repeat run, the intensity of the second peak was found to have grown significantly (Fig. 3b). In a subsequent run following the addition of two further drops of water, only the -108.0 ppm peak was observed (Fig. 3c). Highly siliceous faujasite is hydrophobic and absorbs only about 1% of its weight in water. Therefore, both the oven-dried sample and the sample exposed to air contain very little water. It appears that, under the extreme forces exerted on the sample during magic angle spinning, water added to the sample is forced into the zeolite cavities. It is well known (20) that adsorbed species influence the silicon chemical shifts in zeolites, and in the present system the cavities containing

water have a shift of  $-108.0$  ppm while those without water resonate at  $-108.4$  ppm. The effect is reversible in that drying the hydrated sample results in a spectrum containing only the single peak characteristic of cavities without water.

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