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A Neutron Powder Diffraction Analysis of Potassium-Exchanged Ferrierite

Ferrierite is a versatile catalyst both in hydrocarbon processing and in the petrochemical industry. The H^+-exchanged form of ferrierite has been reported as an efficient catalyst for the hydration of alkenes (*1*), the cracking of *n*-alkanes (*2*), and the isomerization of *m*-xylene to *p*-xylene (*3*). Harrison *et al.* (*4*) have noted that its use in methanol conversion gives appreciably lower aromatic selectivity than ZSM-5, probably because the 10-ring windows of ferrierite (0.42 × 0.54 nm) are smaller in diameter than those of ZSM-5 (0.53 × 0.56 and 0.51 × 0.55 nm). We have found that the *n*-butane cracking rate coefficient (*5*) of H^+-exchanged ferrierite is 3.6 times as great as that of a typical sample of ZSM-5 (*6*). Alkali-metal-exchanged zeolites are at present of considerable commercial significance since they are key components of effective catalysts for the aromatization of alkanes, such as *n*-hexane to benzene. A good example (*7*) is the K^+-exchanged form of zeolite L. We considered, therefore, that a sensible test material for a structural investigation of ferrierite would be the K^+-exchanged form of the zeolite.

The structure of ferrierite was determined by single-crystal X-ray diffraction by Vaughan (*8*) and Kerr (*9*). The framework is characterized by 5-membered rings of $[TO_4]$ tetrahedra (T = Si^{4+} or Al^{3+}), which link up to form a system of intersecting channels in two dimensions. There are 6- and 10-membered ring channels parallel to the *c* axis and an 8-membered ring (0.35 × 0.48 nm) channel parallel to the *b* axis (see Fig. 1). The only data reported for nonframework atoms are for the hydrated form of the zeolite where the cation is Mg^{2+} (*10*).

Apart from their normal vibrational and librational motion, the framework atoms of zeolites remain essentially unchanged during the course of thermal activation and other pretreatments prior to their use as catalysts. The extra-framework cations, however, may undergo pronounced changes in siting, and this makes zeolites particularly amenable to *in situ* investigation by powder diffraction. Previously we have reported the use of high-temperature X-ray studies of Ni^{2+}-exchanged zeolite Y (*11, 12*), and a low-temperature neutron diffraction study of La^{3+}-exchanged zeolite Y (*13*). We have embarked on a study of synthetic powdered samples of this catalyst using the techniques of both neutron and X-ray diffraction, and report in this paper on a neutron Rietveld profile analysis (*14*) of a K^+-exchanged ferrierite.

One of the features of the neutron Rietveld profile analysis is the use of known interatomic distances (or bond distances) in the refinement (soft constraints). Baerlocher *et al.* (*15*) have described this technique and its application to an X-ray profile analysis of as-synthesized ZSM-5. In the present work, the powder neutron diffraction data alone are insufficient to determine the fairly complex structure with an accepted degree of precision, and during refinement without soft constraints the structural model tends toward false minima. In order to overcome this problem, the observation/parameter ratio is increased by adding observed bond distances to the diffraction data. The use of soft geometric constraints ensures that bond lengths (and angles) are kept within chemically sensible ranges during the least-squares procedure.

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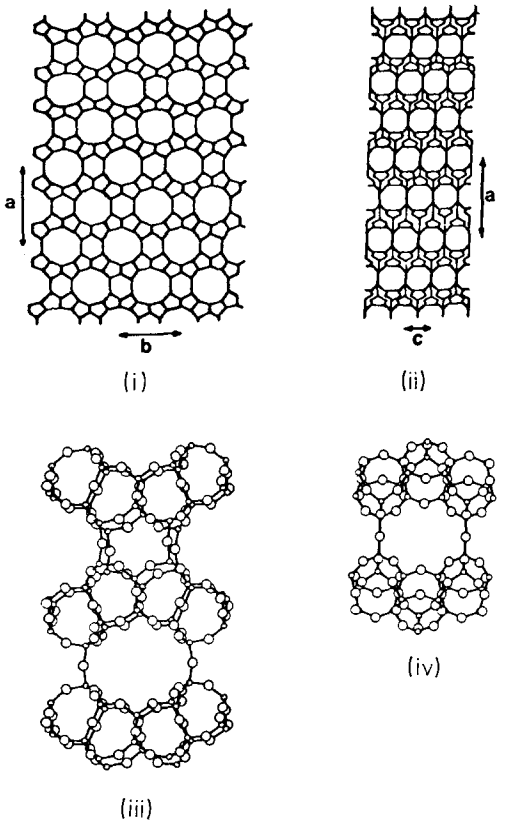

FIG. 1. Views of the structure of ferrierite down (i) the *c* axis showing the 6- and 10-membered rings and (ii) the *b* axis showing the 8-membered ring. Enlarged representations of (i) and (ii) are illustrated in (iii) and (iv), respectively. The view in (iii) has been rotated by 5° around both the *a* and *b* axes relative to (i).

The balance between the two separate contributions to the refinement is maintained by a common weight factor c_w such that the quantity that is minimized in the overall refinement is $S = S_R + c_w S_D$, where S_R is the quantity minimized by the profile fit and S_D is the quantity minimized by the geometric restrictions.

A ferrierite sample containing both Na^+ and K^+ extra-framework cations was kindly provided by Dr. M. F. M. Post of Shell Research, Amsterdam (KSLA). This was ion-exchanged twice with 2 *M* KCl solution giving a material (hereafter referred to as K^+-ferrierite) with a dehydrated unit cell composition of $K_{3.5}Al_4Si_{32}O_{72}$ from chemical analysis. We conclude on the basis of electroneutrality that there are probably some Brønsted acid sites present. Less than 0.1 Na per unit cell were observed from the chemical analysis. ^{27}Al MAS NMR indicated the absence of extra-framework octahedral aluminium, implying that the Si/Al ratio of 8 is applicable to the framework structure. X-ray powder diffraction gave the complex pattern characteristic of a ferrierite structure.

Neutron powder diffraction data of the dehydrated K^+-ferrierite were collected at 4 K at the Institut-Langevin (ILL), Grenoble, using the high-resolution diffractometer, D2B. A surprising aspect of the powder pattern was a background containing broad features at values of 2θ about 48 and 82°.

Rietveld profile analysis was performed using the generalized crystal structure analysis system (GSAS) programme (*16*). Starting coordinates and space group (*Immm*) for the framework were taken from the single-crystal refinement of ferrierite by Vaughan (*8*). Scattering lengths from the GSAS programme were employed: b_O = 0.5805, b_{Si} = 0.4149, b_{Al} = 0.3449 and b_K = 0.367, all in units of 10^{-14} m. The scattering of the tetrahedral atom $b_T = 0.4071 \times 10^{-14}$ m was a weighted average of silicon and aluminium scattering lengths. A 9-parameter real Fourier series was used successfully to fit the complex background. Refinement of the framework model progressed to an R_P value of 8.28%; the *T*–O bond distances, however, were chemically implausible ranging from 1.55 to 1.73 Å. A difference Fourier calculation did not reveal any definitive extra-framework scattering. At this stage, constraints of the *T*–O bond distances were imposed using an ideal bond length of 1.616 + 0.010 Å; this is a weighted value based on bond distances of Si–O and Al–O of 1.60 and 1.74 Å, respectively. The soft-constraint common-weight factor c_w (see above) was adjusted such that all the *T*–O distances refined to between 1.60 and 1.63 Å. A subsequent difference Fourier calculation clearly showed several extra-

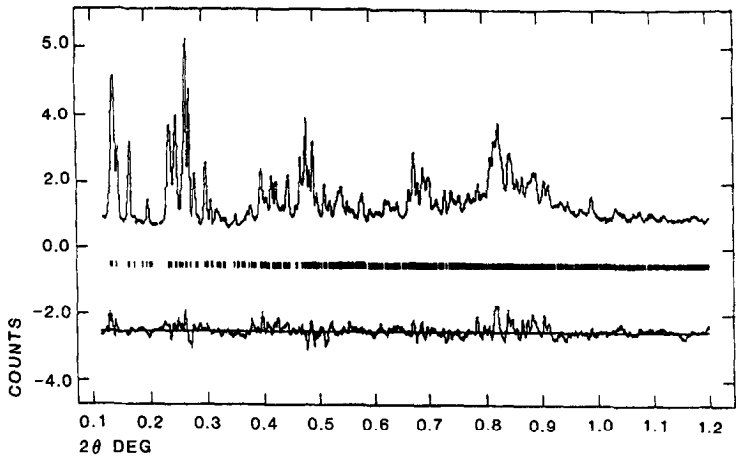

FIG. 2. Observed and difference neutron powder diffraction profiles of K^+-ferrierite. The vertical lines indicate the peaks used in the refinement.

framework positions, and these were *separately* included in the model and refined. Three species were found which gave non-zero occupancies, lower profile values, and chemically sensible positions in the zeolite channels. Two of these were designated K^+ cations since their bond distances to framework oxygen were characteristic of K–O bonds (e.g., nearest-neighbour K^+-bonds in dehydrated K^+-exchanged zeolite A (*17*) range from 2.57 to 2.99 Å). The third atom with a longer bond to the framework was assumed to be an extra-framework oxygen. These three atoms were then added to the model and were refined at the same time. This enabled the common weight factor c_w to be reduced while still keeping the *T*–O distances within the 1.60 to 1.63 Å limit. The final profile (R_p) and weighted profile (R_{wp}) values were 7.83 and 9.92%, respectively (reduced $\chi^2 = 1.23$). Final observed and difference profiles are shown in Fig. 2, and structural details are given in Tables 1 and 2.

This powder profile analysis is the first example of cation location in a dehydrated ferrierite. The results demonstrate the power of using soft constraints in the structural model, without which the refinement generated false minima.

Figure 3 shows the location of the extra-framework species in the channels of K^+-ferrierite. Both the K^+ cations are located in the 10-ring channels, K(1) at the intersection of the 10- and 8-ring channels and K(2) in the plane of the 6-ring; K(2) is not visible down the 8-ring channel. The K^+ cation occupancy per unit cell based on this refinement is 3.34, in good agreement with chemical analysis. The bond valence sums for the K^+ sites in the structure, when computed using the empirical parameters compiled by Brown and Kang Kun Wu (*18*), give values of 0.57 and 0.78 for K(1) and

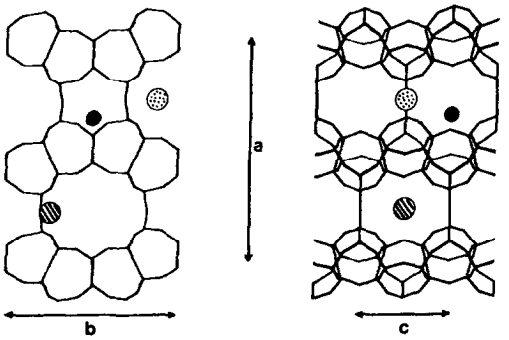

FIG. 3. Location of the extra-framework species in the channels of K^+-ferrierite; ◍, K(1); ○, K(2); ●, O(9).

TABLE 1

Atomic Coordinates, Isotropic Thermal Parameters (B_{iso}) and Occupancies (Number per Unit Cell, n) of Dehydrated K^+-Exchanged Ferrierite

Atom	Symmetry	x	y	z	B_{iso}/A^2	n
$T(1)$	mm2(100)	0.1535(6)	0	0	1.03(9)	4
$T(2)$	m(001)	0.0855(2)	0.2004(5)	0	1.03(9)	8
$T(3)$	m(010)	0.2764(3)	0	0.2879(7)	1.03(9)	8
$T(4)$	1	0.3260(2)	0.2034(2)	0.2002(7)	1.03(9)	16
O(1)	mm2(010)	0	0.1887(11)	0	3.42(8)	4
O(2)	mm2(100)	0.2536(8)	0	$\frac{1}{2}$	3.42(8)	4
O(3)	m(001)	0.0989(5)	0.0879(5)	0	3.42(8)	8
O(4)	m(010)	0.2010(4)	0	0.1813(11)	3.42(8)	8
O(5)	-1	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	3.42(8)	8
O(6)	m(010)	0.1457(5)	0.2718(7)	$\frac{1}{2}$	3.42(8)	8
O(7)	1	0.1103(3)	0.2553(5)	0.1783(7)	3.42(8)	16
O(8)	1	0.3228(4)	0.0919(3)	0.2367(9)	3.42(8)	16
K(1)	mm2(010)	0	0.244(3)	$\frac{1}{2}$	3.42(8)	2.14(12)
K(2)	mm2(010)	0	0.369(6)	0	3.42(8)	1.20(12)
O(9)	mm2(100)	0.072(4)	0	$\frac{1}{2}$	3.42(8)	0.55(8)

Note. Refinement parameters: $R_{wp} = 9.92$, $R_p = 7.83$; $a = 18.651(4)$, $b = 14.173(3)$, $c = 7.404(17)$ Å; $U = 3.3(10) \times 10^2$, $V = 6(10) \times 10^1$, $W = 2.9(2) \times 10^2$; asymmetry parameter = $1.25(5) \times 10^1$; number of variables = 48; range refined = 11.5 – 120° 2θ; space group is *Immm*; B_{iso} values for T atoms constrained to be equivalent; B_{iso} values for O and nonframework atoms similarly constrained.

K(2), respectively (theoretical value 1.00). These rather low values are comparable to bond valence for K^+ cations in other zeolites, e.g., K^+-exchanged gallo-zeolite L (*19*) yields values of 0.85, 0.54, and 0.59. These figures reflect the poor coordination geometries that are found around the cations in dehydrated zeolites.

The third extra-framework species, O(9), has a lower occupancy than K(1) and K(2) and is situated in the cavity at the intersection of the 6- and 8-ring channels. It was not designated as a potassium because, as mentioned earlier, the O(9)–O(4) and O(9)–O(2) distances are too long to be K–O bonds. In any case, it would make the K^+ occupancy of the structure too large compared with that of the chemical analysis. Since MAS NMR rules out nonframework aluminium, we suggest that it is an oxygen atom, probably hydrogen-bonded to the framework oxygens, and perhaps involving a hydroxonium component. Infrared spectroscopy at 4 K on the same dehydrated sample might clarify this point, as would a neutron-based study on deuterated samples.

The present results allow us to draw some provisional conclusions relating to the catalytic potential of K^+-ferrierite. The placement of K(1) in the 8-ring window, with substantial occupancy, will hinder the diffusion of molecules from one 10-ring channel to the next. It would indeed be attractive to identify O(9) as a possible active site, but the restricted access to this position, via the 8-ring window, makes this unlikely. Thus, K^+-ferrierite, like zeolite L, is essentially a one-dimensional system, although the main channel is not only smaller than zeolite-L, but it is made more so by the location of K(2). (In zeolite L extra-framework cations reside in shallow pockets that line the channels, thus keeping the latter relatively accessible compared with those of a cation-exchanged ferrierite). Hence the diffusion and catalytic reactions of hydro-

TABLE 2

Interatomic Distances (Å) and Angles (°) of Dehydrated K^+-Exchanged Ferrierite

T–O bond distances	
T(1)–O(3) × 2	1.609(3)
T(1)–O(4) × 2	1.608(3)
T(2)–O(1)	1.603(4)
T(2)–O(3)	1.615(4)
T(2)–O(7) × 2	1.601(3)
T(3)–O(2)	1.628(4)
T(3)–O(4)	1.613(4)
T(3)–O(8) × 2	1.609(3)
T(4)–O(5)	1.607(4)
T(4)–O(6)	1.613(4)
T(4)–O(7)	1.600(4)
T(4)–O(8)	1.603(4)
Mean *T*–O distance	1.609
T–O–*T* angles	
T(2)–O(1)–*T*(2)	168.0(1)
T(3)–O(2)–*T*(3)	149.6(1)
T(1)–O(3)–*T*(2)	149.7(7)
T(1)–O(4)–*T*(3)	152.7(9)
T(4)–O(5)–*T*(4)	180.0(0)
T(4)–O(6)–*T*(4)	133.7(7)
T(2)–O(7)–*T*(4)	148.9(5)
T(3)–O(8)–*T*(4)	149.0(5)
Extra-framework atoms	
K(1)–O(6) × 2	2.746(11)
K(1)–O(7) × 4	3.152(7)
K(1)–O(1) × 2	3.783(10)
K(2)–O(1)	2.56(9)
K(2)–O(7) × 4	2.93(5)
K(2)–*T*(2) × 2	2.88(7)
O(9)–O(4) × 2	3.37(5)
O(9)–O(2)	3.38(8)
O(9)–O(9)	2.69(15)

carbons in K^+-ferrierite must take place in the 10-ring channels of the framework.

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REFERENCES

1. Eguchi, K., Tokiai, T., Kimura, Y., and Arai, H., *Chem. Lett.*, 567 (1986).
2. Kibby, C. L., Perrotta, A. J., and Massoth, F. E., *J. Catal.* **35,** 256 (1974).
3. Seddon, D., *J. Catal.* **98,** 1 (1986).
4. Harrison, I. D., Leach, H. F., and Whan, D. A., *Zeolites* **7,** 21 (1987).
5. Rastelli, H., Lok, B. M., Duisman, J. A., Earls, D. E., and Mullhaupt, J. T., *Canad. J. Chem. Eng.* **60,** 44 (1982).
6. Maddox, P. J., Yan Xu, and Thomas, J. M., unpublished work.
7. Barnard, J. R., *in* "Proceedings, Fifth Intl. Conf. on Zeolites, Naples, 1980" (L. V. C. Rees, Ed.), p. 686. Heyden, London, 1980.
8. Vaughan, P. A., *Acta Crystallogr.* **21,** 983 (1966).
9. Kerr, I. S., *Nature (London)* **210,** 294 (1966).
10. Mortier, W. J., "Compilation of Extra Framework Sites in Zeolites." Intl. Zeol. Assoc., Butterworths, London, 1985.
11. Maddox, P. J., Stachurski, J., and Thomas, J. M., *Catal. Lett.* **1,** 191 (1988).
12. Thomas, J. M., Williams, C., and Rayment, T., *J. Chem. Soc. Faraday Trans. 1* **84,** 2915 (1988).
13. Cheetham, A. K., Eddy, M. M., and Thomas, J. M., *J. Chem. Soc. Chem. Comm.*, 1337 (1984).
14. Rietveld, H. M., *J. Appl. Crystallogr.* **2,** 65 (1969).
15. Baerlocher, C. H., Heppard, A., and Meier, W. M., DLS-76, "A Program for the Simulation of Crystal Structures by Geometric Refinement." Inst. of Crystallography, ETH, Zurich, 1978. See also, Baerlocher, C. H., Intl. Congr. on Crystallography, Perth, 1987.
16. Larson, A. C., and von Dreele, R. B., "Generalized Crystal Structure Analysis System." Los Alamos National Laboratory, Los Alamos, NM.
17. Pluth, J. J., and Smith, J. V., *J. Phys. Chem.* **83,** 741 (1979).
18. Brown, I. D., and Kang Kun Wu, *Acta Crystallogr. B* **32,** 1957 (1976).
19. Wright, P. A., Thomas, J. M., Cheetham, A. K., and Nowak, A. K., *Nature (London)* **318,** 611 (1985).

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