Probing the Structure of Zeolites by Fourier Transform Electron Microscopy: Zeolite-L as a Test Case

G. Robert Millward,[a] John M. Thomas,[a] and Robert M. Glaeser[b]

[a] *Department of Physical Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EP, U.K.*
[b] *Department of Biophysics, University of California, Berkeley, California 94720, U.S.A.*

The structures of zeolites cannot readily be determined by *X*-ray methods chiefly because only microcrystalline samples are available: a new method of obtaining projected structures, based on low-dose electron microscopic imaging, is described and illustrated for the [00.1] projection of zeolite-L.

Although high-resolution electron microscopy (HREM) has added significantly to our knowledge of the microstructure of zeolites[1] and, in particular, has proved uniquely valuable both in characterizing intergrowths at the sub-unit cell level[2—5] and in providing 'model' structures for recently discovered[6] zeolites, it suffers from one troublesome disadvantage: the materials to be investigated must not deteriorate structurally during electron bombardment. Whilst much can be done to improve beam stability either by operating at high accelerating voltages (and) or by rendering the samples less prone to beam damage by prior dealumination, many, as-prepared zeolites (and several other materials) are not conveniently amenable to conventional HREM owing to their tendency to distintegrate on a time scale short by comparison with that required to accumulate an adequate signal for image formation. Typically, to obtain a high-resolution image of acceptable contrast a 2.8 s exposure to an incident flux of 65 electrons $Å^{-2}\ s^{-1}$ at 200 KeV is required; and this is too much for most zeolites. As there has been a sharp increase in the number of new zeolites, the structures of which have so far defied characterization, there is a pressing need for a more widely applicable method of identifying projected structures of zeolites.[7] In this com-

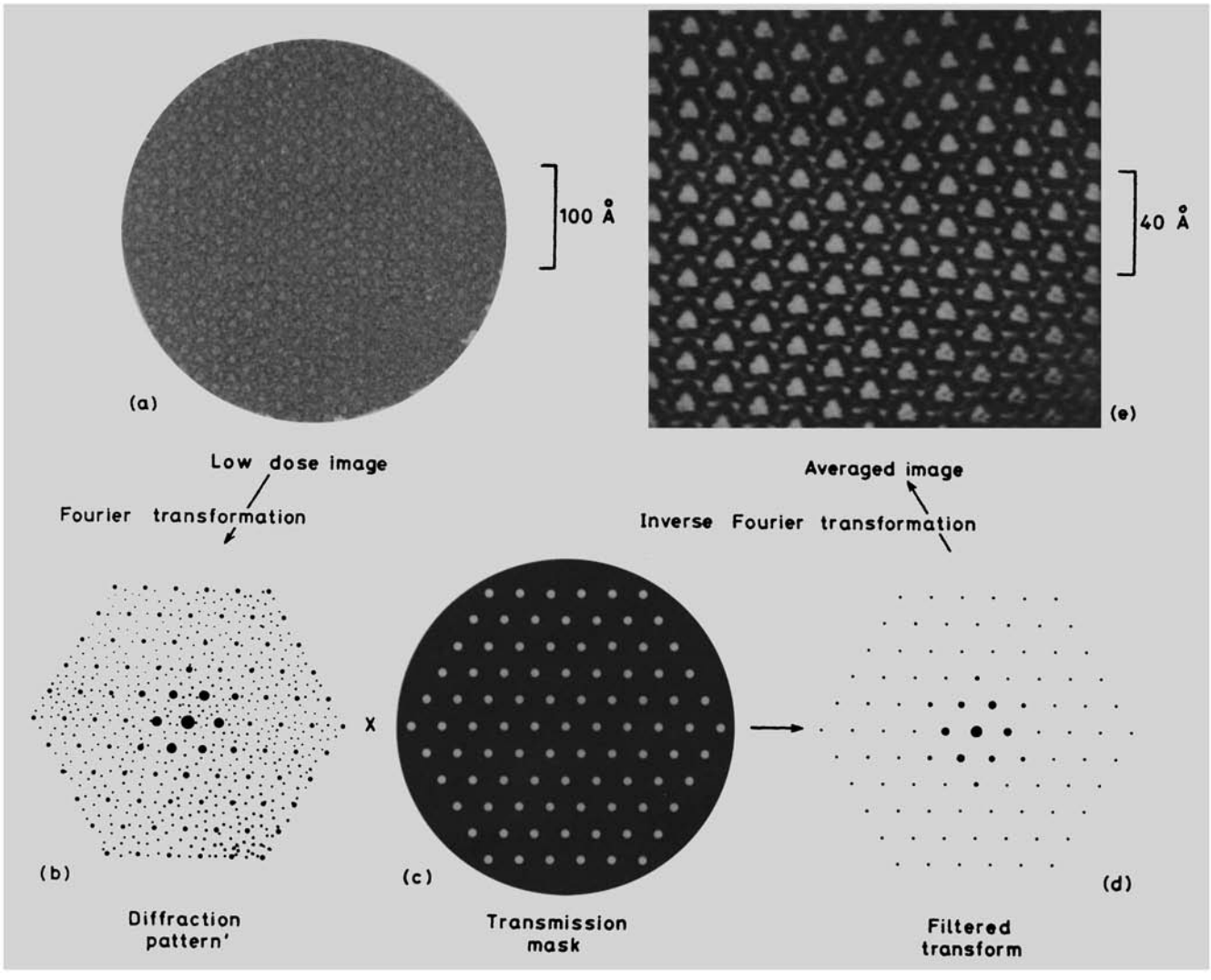

Figure 1. (a) Low-dose (exposure of 11 electrons $Å^{-2}$) image of zeolite-L recorded on Agfa Scientia 23D56 film at an original magnification of 123 000. Usually to record an HRE micrograph of good contrast under otherwise indentical conditions would require an exposure of 180 electrons $Å^{-2}$. (Printed on Ilfospeed paper, grade 5.) Projection along [00.1]. (b) Schematic diagram of the 'noisy' diffraction pattern calculated by a process of two-dimensional Fourier transformation of the digitized version (obtained by optical microdensitometry) of (a). (c) Schematic diagram of the filter (transmission mask) by which the transform (b) is multiplied to yield (d). This mask was generated by an interactive computer program, and the holes (white dots) were chosen to have a Gaussian transmission profile of half-width equal to a fifth of the separation of the *h k o* array in the transform. (d) Schematic illustration of filtered transform. [The background noise, visible in (b) has now been eliminated.] (e) Averaged (improved) image formed by an inverse digital Fourier transformation of (d) (printed on Ilfospeed paper, grade 1).

munication we describe how good progress can be made in extracting the key features of the channel structure of a zeolite by adapting a methodology that has been developed[8,9] by molecular biologists for structural investigation of beam-sensitive biological membranes and crystals. We illustrate the technique using a sample of zeolite-L, which, although partially de-aluminated, still presents significant problems for imaging at resolutions approaching 3.0 Å[3]. Zeolite-L has considerable potential as a catalyst in the petrochemical industry.

In essence, the method consists, first, of recording a low-dose image, such as that shown in Figure 1(a), where the contrast is too poor to yield any useful, real-space structural information (2.8 s exposure to an incident flux of 4 electrons $Å^{-2}$ s^{-1}). Then, after converting this image by optical densitometry into its digitized analogue, to calculate the corresponding Fourier transform [*i.e.* diffraction pattern, Figure 1(b)] which, on multiplication by an appropriate mask, Figure 1(c), yields a cleaner (less 'noisy') diffraction pattern, Figure 1(d), that, on inverse Fourier transformation, gives the desired, improved image Figure 1(e).

What we have done in proceeding from Figures 1(a) to 1(e) is to take a convolution of the original image with the Fourier transform of the filter mask, the latter function being the product of the real-space lattice, and the Fourier transform of a single mask (or hole) function. Progression from Figure 1(a) to 1(e) is, therefore, a local averaging process.[10] And for the particular conditions that obtain here we have, in the course of effecting the improvement, utilized an averaging factor (the number of superimpositions) of *ca.* 23.

The averaged image, Figure 1(e), reveals much detail that is invisible in the low-dose precursor. The large white spots correspond to the projections of the apertures of the 12-membered channels that run in the [00.1] direction; and the fine-structure surrounding each large spot, although a little distorted, corresponds to the six- and eight-membered chan-

nels known[3] to run through the structure. (At this stage it is premature to speculate about the significance of the apparent 3-fold, rather than the expected[3] 6-fold, symmetry.) To retrieve more structural information one can envisage the possibility of utilizing the above methodology but with the sample inclined at a series of angles to the primary beam.[8,9,11,12] Reconstruction, following local procedures such as those that have proved successful for a range of biological macromolecules (*e.g.* viruses, microtubules, muscle filaments, ribosome crystals, and enzymes), would then yield the full, three-dimensional structure. But the recording of even a few improved images down two or three high-symmetry directions coupled with additional information derived from electron diffraction and magic-angle-spinning n.m.r.[13] constitutes an effective method of elucidating the structure of zeolites.

We thank Drs. R. Henderson, H. E. Huxley, A. Klug, and E. Egelman of the M.R.C. Laboratories, Cambridge, for their kindness in letting us use computer image processing facilities. We also thank B.P. and the S.E.R.C. for financial support and Dr. D. A. Jefferson for discussion.

Received, 19th April 1985; Com. 520

References

1 J. M. Thomas, Proceedings of the 8th International Congress on Catalysis, Berlin, 1984, Verlag Chemie, 1984, vol. 1, p. 31.
2 J. M. Thomas and G. R. Millward, *J. Chem. Soc., Chem. Commun.*, 1982, 1380.
3 O. Terasaki, J. M. Thomas, and S. Ramdas, *J. Chem. Soc., Chem. Commun.*, 1984, 216; O. Terasaki, J. M. Thomas, and G. R. Millward, *Proc. R. Soc., London, Ser. A.*, 1984, **395**, 153.
4 G. R. Millward, S. Ramdas, and J. M. Thomas, *Proc. R. Soc. London, Ser. A*, 1985, **399**, 57.
5 J. V. Sanders, *Zeolites*, 1985, **5**, 81.
6 S. A. I. Barri, G. W. Smith, D. White, and D. Young, *Nature*, 1984, **312**, 533.
7 J. M. Thomas, *Ultramicroscopy*, 1982, **8**, 13.
8 A. Klug, *Chemica Scripta*, 1978—79, **14**, 245.
9 P. N. T. Unwin and R. Henderson, *J. Mol. Biol.*, 1975, **94**, 425.
10 R. D. B. Fraser and G. R. Millward, *J. Ultra Structure Res.*, 1970, **31**, 203.
11 R. Henderson and P. N. T. Unwin, *Nature*, 1975, **257**, 28.
12 R. M. Glaeser, 'Electron Crystallography of Biological Macromolecules,' *Ann. Rev. Phys. Chem.*, in the press.
13 J. M. Thomas, J. Klinowski, S. Ramdas, B. K. Hunter, and D. T. B. Tennakoon, *Chem. Phys. Lett.*, 1983, **102**, 158.