Direct, Real-space Determination of Intergrowths in ZSM-5/ZSM-11 Catalysts

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The performance of shape-selective catalysts is thought to be a function of the nature of the intergrowths present in the structure, but hitherto no direct methods of identifying isolated or ordered intergrowths have been available; high resolution electron microscopy is shown to be capable of solving such problems, and in particular single strips of ZSM-11 may be directly identified in ZSM-5.

ZSM-5, one of the most important industrial shape-selective catalysts, is capable, *inter alia*, of cracking C–C bonds in long-chain n-paraffins but not in those with side chains, of converting methanol into petrol (gasoline), and of producing ethylbenzene from a feedstock of benzene and ethylene.[1–3] Since single crystals of this highly siliceous zeolite (Brønsted acid) catalyst cannot be readily prepared, its structure has been deduced, by Kokotailo *et al.*,[1] from model-building and other approaches that utilize powder *X*-ray diffraction and gas-sorption measurements. Although some doubt currently exists[5] as to the correct assignment of space group, it is known that ZSM-5 consists of a system of two intersecting channels (diam. *ca.* 5.5 Å); those that run along the *b* axis are straight and circular whereas those that are parallel to *a* are sinusoidal and of elliptical cross-section.[6] The structure itself is made up of linked SiO_4 and AlO_4 tetrahedra, and may be pictured as being composed of (100) slabs (*i.e.* sheets parallel to *b*) that are related by inversion (*i*) as shown in Figure 1.

ZSM-11, also an important shape-selective catalyst,[7] differs from ZSM-5 in that an individual (100) slab is a mirror image (σ) of its neighbour in the *x* direction. This difference results in there being two linear intersecting channels in ZSM-11. The performance of these shape-selective catalysts is crucially governed by the size and nature of the cavities formed

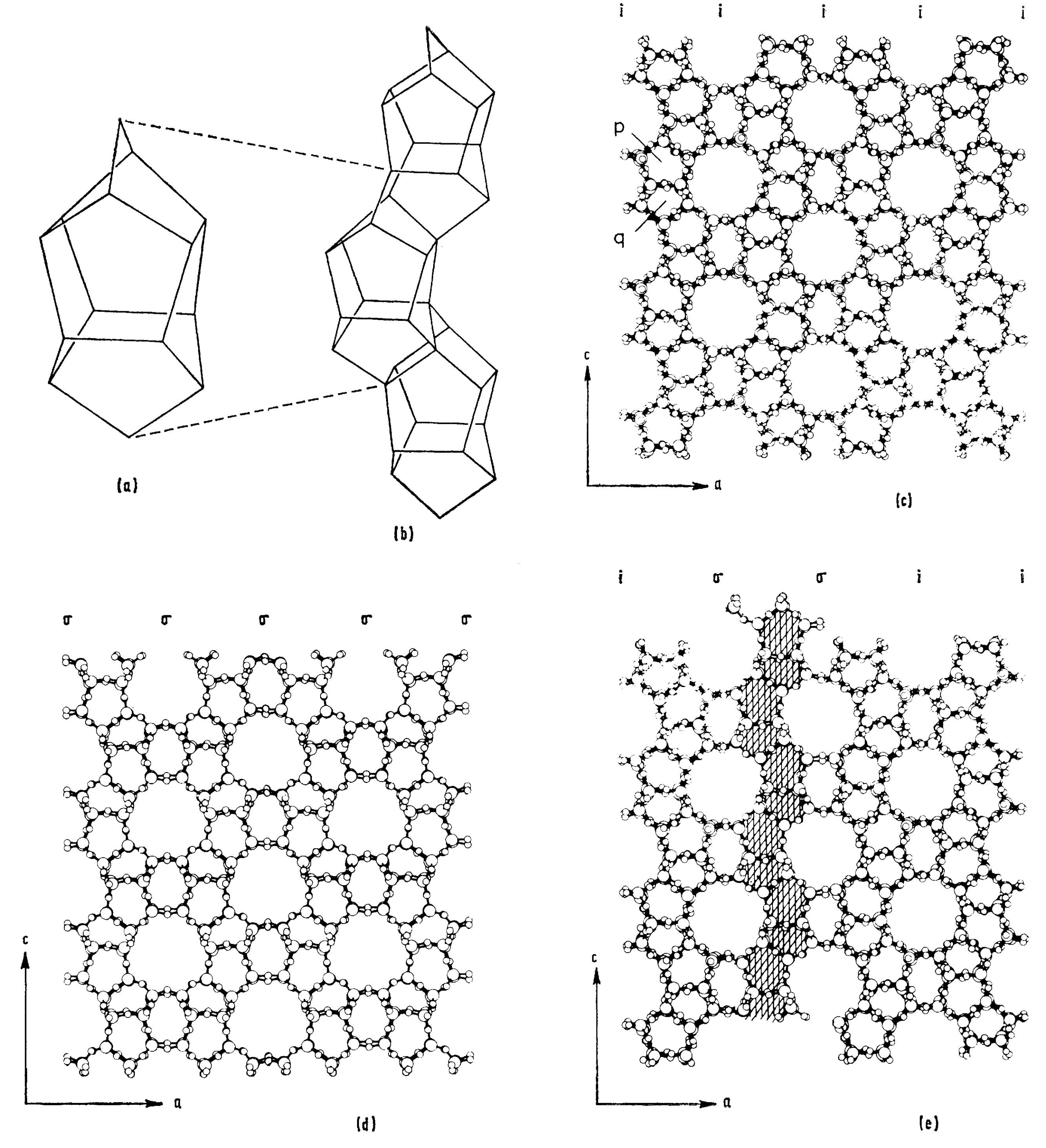

Figure 1. (a) Segment of the structure of ZSM-5 and ZSM-11 showing connected 5-membered rings composed of linked tetrahedra (SiO_4 and AlO_4). Each connecting line represents an oxygen bridge. (b) The chains from which the ZSM-5 and ZSM-11 structures are built are themselves made up by linking the units shown in (a). (c) In ZSM-5 chains are linked such that (100) slabs are related by inversion (i). (d) In ZSM-11 chains are linked such that (100) slabs are mirror images (σ) of one another. (e) Representation of intergrowth of ZSM-5 and ZSM-11. p and q refer, respectively, to the larger and smaller 5-membered rings. (The rings are in reality of equal size, but do not appear so in projection).

at the channel intersections, since these are the factors that determine the volume and shape of the transition states and products that may be formed[3,7] selectively within these catalysts. In ZSM-5 the cavities are all equivalent. In ZSM-11, on the other hand, they are of two types: one is very nearly the same as that which occurs in ZSM-5, and the other has *ca.* 30% additional volume.

It has been suspected for some time that, in specific preparations of ZSM-5, there may be intergrown regions of ZSM-11, and it has been argued[8] that there exists a large family of

(c)

(b)

(a)

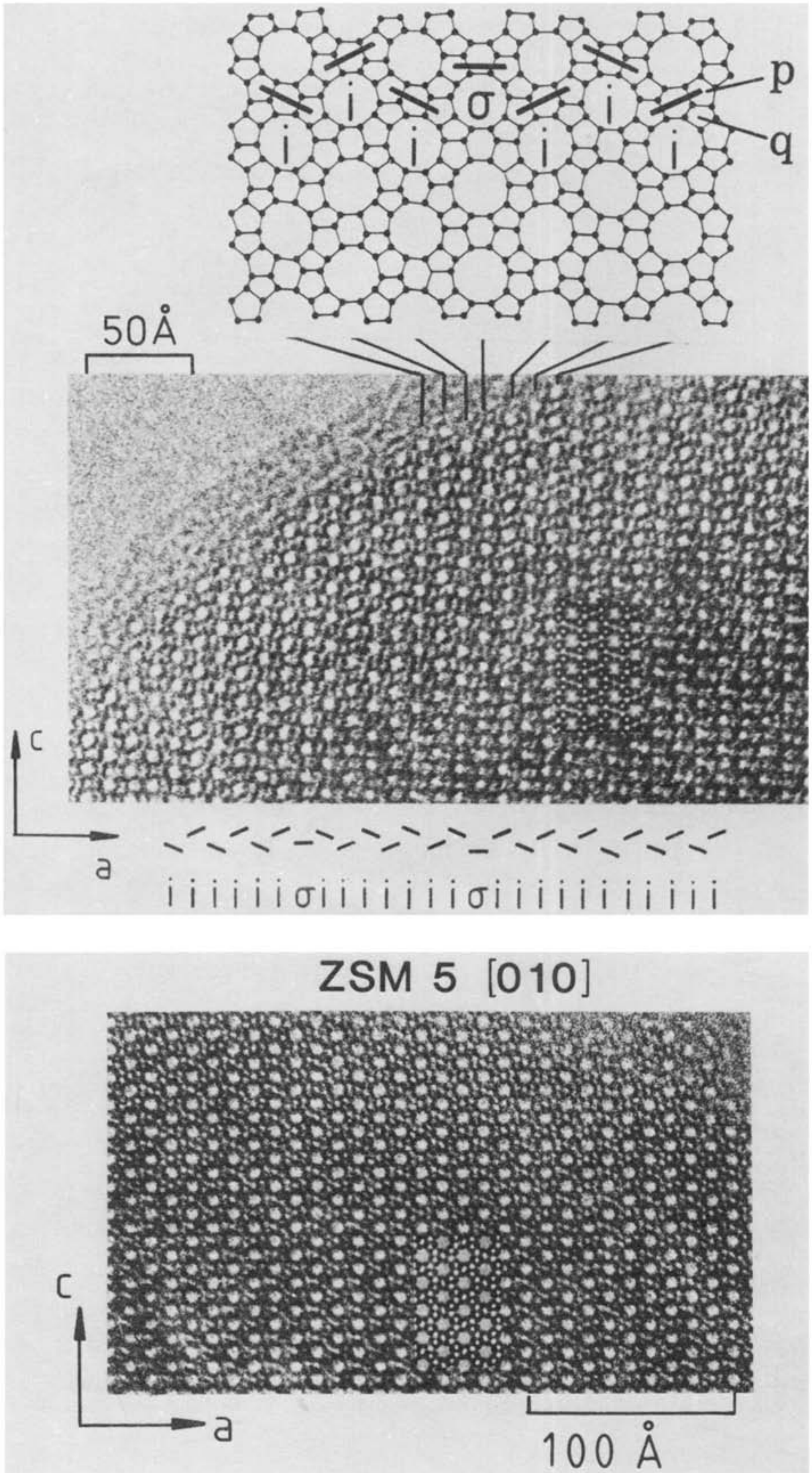

Figure 2. (a) Ultra high-resolution (real-space) image of a highly ordered ZSM-5 crystal viewed along the *b* axis. The calculated image[10] is shown in the inset. (b) Real-space image of a typical ZSM-5 catalyst containing two narrow, separated strips of intergrown ZSM-11. [See (c) and text]. (c) Interpretation of (b). By following the pattern generated by the lines connecting the larger (p-type) 5-membered rings, the local structure may be easily read off. Zig-zag lines signify ZSM-5; horizontal lines, ZSM-11.

regular intergrowth structures with ZSM-5 and ZSM-11 as end members. For both the regular and irregular intergrowths, as well as for random, 'isolated' intergrowths, *direct* experimental evidence has been lacking, there being few techniques capable of solving this problem. We here describe how ultra-high-resolution electron microscopy[9] enables the structural components to be read off directly at the sub-unit-cell level of discrimination.

Figure 2(a) is a high-resolution microscopic image of a highly ordered, crystalline† region of ZSM-5 together with the calculated[9,10] image. The 10-membered, 6-membered, and 5-membered rings are clearly visible. Although it is not possible routinely to distinguish, in images of this quality, the difference between the larger and smaller 5-membered rings [marked *p* and *q* respectively in Figures 1(c) and 2(c)], the eye readily discerns the line connecting two larger 5-membered rings (see Figure 2(c)]. This enables the difference between ZSM-5 and ZSM-11 to be readily identified even when less than a unit cell width of one is intergrown within the other. It, therefore, means that provided care is taken in recording representative microscopic images under optimal defocus conditions (see ref. 9), a direct technique now exists for determining the ultrastructure of the ZSM-5/ZSM-11 family of shape-selective catalysts. We have evidence, which we shall publish fully elsewhere,[11] of extended strips of semi-regular growths, the repeats being sufficiently pronounced as to be rendered 'visible' by an optical diffractomeric analysis[12] of the high-resolution images.

† The image shown in Figure 2(a) is of a sample kindly provided by Drs. M. Barlow and D. Stewart of B.P., Sunbury. The image shown in Figure 2(b) is of a ZSM-5 catalyst sample kindly provided by Dr. P. B. Weisz, Mobil Co., Princeton.

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